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ENGINEERING ANALYSIS
OF
EMISSIONS CONTROL TECHNOLOGY
FOR
SULFURIC ACID MANUFACTURING PROCESSES

FINAL REPORT UNDER CONTRACT CPA 22-69-81
FOR
DIVISION OF PROCESS CONTROL ENGINEERING
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
PUBLIC HEALTH SERVICE
U.S. DEPARTMENT OF HEALTH, EDUCATION & WELFARE

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I

ABSTRACT

The findings of this report cover three areas -- the capabilities of various control systems and their state of development, the cost of emission control, and the limitations of present systems, with recommendations for areas of further study to achieve better control effectiveness and process reliability at lower control cost.

Existing plants can reduce their emissions somewhat by modifying their operating conditions with little capital expenditure, but this control is limited to about 2,000 ppm of SO_2 . Present technology can achieve a control effectiveness of 500 ppm of SO_2 via the dual absorption route, and excellent acid mist control in the order of 0.1 mg/SCF. No fully developed acid plant control systems are commercially operated in the U.S. which achieve an effectiveness of 100 ppm of SO_2 , but there are promising ones in various stages of development.

It is doubtful that there is any contact plant in the U.S. to which some type of control system could not be applied to reduce emissions to < 500 ppm SO_2 , but to do so economically may be a different story.

Cost of emission control varies widely with plant capacity, type of control system and other factors. Cost of < 500 ppm SO_2 control for a 250 T/D contact plant varies from about \$.75 to over \$3 per ton of acid. Mist control costs vary from \$.02 to \$.35/tons of acid. These costs are predicated on an assumption that promising processes will work as expected. Control cost is lower for large plants.

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Recommended areas for study include development of resin and molecular sieve adsorbents, oxidation inhibitor development for tail gas recovery processes, study of stack dispersion and factors affecting it, plus development work on several processes, both for treatment of tail gas and improved in-plant conversion.

II

INTRODUCTION

The typical design conversion efficiency of recently built sulfuric acid plants is 98%. If this design efficiency were maintained the exit gas concentration of SO_2 would be 2,000 ppm or less. Frequently, however, emissions of 3,000-4,000 ppm and more are encountered in actual practice. Control regulations of < 500 ppm SO_2 are being discussed in some areas of the country, which indicates a considerable gap between present practice and proposed control levels.

Sulfuric acid capacity in the United States totals some 38 million short tons per year produced in about 250 plants, of which about 215 are of the contact type, the remainder being of the older chamber type. Perhaps 30% of these plants have some oleum production capacity. A census of the sulfuric acid plants in the United States appears in Part III. Also included in this census are sulfuric acid concentrators of the drum type. Actual production was about 28,500,000 ST in 1968.

Sulfuric acid is produced in a great variety of concentrations and in four grades - commercial, electrolyte or high purity, textile, (having low organic content,) and C.P. or reagent grade. Many of the industries which use sulfuric acid do not actually consume the acid but change its form. In some cases, regeneration to acid is economical, in others it is not. Industries which are the principal users of sulfuric acid include: the wet process phosphoric acid industry which is on the route to produce many phosphate fertilizers, in petroleum refining, the production of alcohols, the production of titanium dioxide for pigments, in the

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production of ammonium sulfate, and in the production of normal super-phosphate (the usual use of chamber acid which is more dilute than the acid normally produced by contact plants) also, iron and steel pickling, caprolactam, production of surface active agents, production of methylmethacrylate, production of hydrofluoric acid and the production of aluminum sulfate. Industries which do not use up the sulfur values are petroleum refining and alcohol production where the actual consumption of the sulfur values is approximately 10% of the total quantity of acid used, the remainder being supplied from regenerated or reconstituted acid produced from dilute acid from the plant operation. Large amounts of dilute sulfuric acid recovered from smelter operations are also used in leaching operations to produce ore concentrates used in the smelters.

Most acid of all grades is consumed near the point in which it is produced; either by the manufacturer or by nearby industries. Very little acid is shipped more than 200 or 300 miles from the point at which it is made.

NAPCA has selected certain industrialized areas in the United States as Air Quality Control Regions (AQCR). The geographic boundaries of each region within an initial group of 57 are to be designated by about mid-1970. As of March 1, 1970, 28 of these have been so designated. The AQCRs are identified by the central cities of the metropolitan areas which they include.

Approximately 40% of the sulfuric acid plants in the United States producing about 1/3 of the annual H_2SO_4 production are located within these 57 AQCRs.

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Problems arising from sulfuric plants are not due to the total quantity of SO_2 and acid mist which they discharge to the atmosphere because these are relatively small. Problems are generally localized and caused by relatively high percentages of SO_2 and/or acid mist (up to 1/2%) combined with relatively low tail gas temperatures and often short stacks which result in poor dispersion. The result is ground level concentrations of SO_2 and mist which may exceed desirable limits in the immediate vicinity of a plant, especially during adverse atmospheric conditions.

Recognizing that more effective control for both existing and new plants will be required in the near future, the Division of Process Control Engineering (DPCE) of the National Air Pollution Control Administration (NAPCA) financed this study by the Consulting Division of Chemical Construction Corporation (Chemico) to evaluate the capabilities and state of development of the available processes and devices to effect this control, to determine the cost of control by various methods, and to outline programs for further development of systems which appear to have the greatest overall potential for reducing undesirable emissions from sulfuric acid plants in the United States at the lowest cost.

The scope of the study is defined in Contract CPA 22-69-81 dated May 23, 1969 between NAPCA and Chemico.

Objectives of the Study

Information developed in this study is intended to provide a basis for management decisions by DPCE in determining the extent and direction which their efforts should be taking in the support and management of research and other programs for control of emissions from sulfuric acid plants and possibly other sources.

To this end, Chemico from its extensive background in the design and construction of all types of sulfuric acid plants has compiled background information on their characteristics and operating conditions. A literature search was made to identify as many methods as possible for emission control including systems normally applied to other stationary sources which might be applicable to the conditions found in sulfuric acid plants.

Sulfuric acid plants were classified into groups having similar problems, to which certain types of control systems might be applied. To make use of the classification it was necessary to compile a census of sulfuric acid plants which are presently in operation in the United States.

After an initial screening to remove the less effective, less applicable and most costly systems from further consideration, the effectiveness and cost of control of selected methods was determined for various classifications to which they could be applied. This process identified the characteristics of the most promising systems, and their limitations,

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and reviewed these with respect to the foreseeable trends in emissions regulations.

Where technology is incomplete, recommendations for development programs have been prepared.

Limitations of the Report

The report is based almost in its entirety upon information available within the Chemico organization. Some proprietary processes for which costs and capabilities have not been disclosed have been evaluated on available information.

It is not the intent of the report to identify the capacity or emission level of any existing plant. The census, classification and capacities of plants have been used to determine the approximate number of potential applications for various processes as a measure of relative merit.

Plan of the Report

The report is presented in two volumes, the first volume being the report itself, and the second containing the literature search.

Volume one is divided into Parts I through VIII. Part I is an abstract summarizing the report and its findings, and Part II the introduction, presenting the purpose of the study, its limitations and the organization of the report; Part III discusses the characteristics of operation and emissions of the various types of sulfuric acid plants, present emission control practice and the expected emission levels of future plants using dual absorption or add-on control techniques. Also included in Part III is the sulfuric acid plant census in Tables 4, 5 and 6.

Part IV lists all processes which were reviewed in preparation of the report, a discussion of control effectiveness, the method of selection of the processes chosen for detailed review, factors effecting reliability of processes and the rationale for selection of the control levels which are used to divide the several processes into categories based upon their capabilities. Also included are descriptions of various processes illustrated by flow diagrams.

The economics of the various processes and devices are covered in Part V, including definitions and selection of parameters used in the economic comparisons. Capital costs for the various processes studied are given, and these with operating costs for the various types of H_2SO_4 plants are used to derive control costs for various processes. Curves of the

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variation of control cost with plant capacity and variation of control cost with control effectiveness also are included, together with a discussion of the factors influencing control cost and effectiveness.

Part VI includes a discussion of the effect of utilization of recovered sulfur values from various other sources upon the sulfuric acid industry. This is illustrated by flow diagrams, process descriptions, capital and operating costs.

Part VII presents the results of the study, including the limitations of the various processes, and outlines programs for development of potentially promising processes or parts of processes.

Part VIII is the Appendix which includes supporting data, including capital cost estimates for various processes and calculations of operating costs for the several processes as applied to different types of H_2SO_4 plants.

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- . Norton Co.
for information on molecular sieves (ZEOLON)

III

SULFURIC ACID PLANTS -
OPERATING METHODS AND GASEOUS EMISSIONS

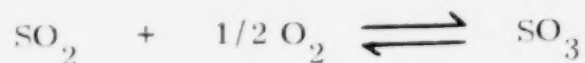
Atmospheric emissions from sulfuric acid plants vary, both in quantity and composition, depending upon the process, the mode of operation of the plant and the condition of the plant. All emissions which are of any concern, however, emanate from one source - the tail-gas stack of the plant, regardless of size, type, or acid grade produced. The qualitative and quantitative emissions of the various classes of plants are fully described in Part III-B.

A. FUNDAMENTAL AND OPERATIONAL CONSIDERATIONS

Emissions of objectionable sulfur compounds from sulfuric acid plants result from either incomplete conversion of the sulfur source to H_2SO_4 , or from carry over of acid mist and droplets formed or entrained in the tail gas. The quantity of SO_2 present in the tail gas is a very small fraction of the total flow, usually less than 1%.

Converter Design Considerations

The basic contact plant reaction:



is a classic example of a reversible, exothermic, catalytic reaction. The thermodynamics of the reaction has been thoroughly described by Duecker and West⁽¹⁾ among others.

- (1) Duecker W.W. and West J.R., "The Manufacture of Sulfuric Acid", Reinhold (1959) pp. 135-185.

The reaction is carried out in a converter in the presence of catalyst containing V_2O_5 . The SO_3 yield is governed by chemical equilibria and kinetics. Due to the adiabatic conditions and the liberation of reaction heat (42,342 Btu/lb mol @ $77^\circ F$) the temperature of the reacting gas mixture rises until the composition of the gas approaches the equilibrium conversion, and heat must be removed if further reaction is required. From this it is obvious that with lower feed temperatures higher conversions may be attained, but will be accompanied by lower reaction rates.

At lower reaction rates catalyst requirements increase thus increasing the pressure drop through the catalyst bed, and resulting in higher operating costs; hence there is an optimum balance between higher conversions and lower catalyst requirements, both dependent upon temperature. The usual commercial practice is to use feed temperatures of $820-840^\circ F$ in three or four stage converters with 160-180 liters of catalyst per daily ton of H_2SO_4 product, overall SO_2 conversion being 95-98%. Below $820^\circ F$ the reaction rate slows down until it is negligible around $750^\circ F$. However, low temperature catalysts are available which are useful at $750^\circ F$.

The initial step in the design of a converter is to determine the reaction path by constructing an equilibrium conversion diagram. Such a diagram is shown in Figure 1, for a typical feed gas composition of 8% SO_2 , 13% O_2 and 79% N_2 . The data required for the construction are values for equilibrium constant, heats of formation and enthalpies of the gaseous components. For the SO_2 oxidation reaction:-

$$K_p = \frac{(P_{SO_3})}{(P_{SO_2}) (P_{O_2})^{1/2}} \quad \text{where } P = \text{component partial pressure}$$

at one atmosphere total pressure

$$K_p = \left(\frac{SO_3 \text{ Mols/Hr}}{SO_2 \text{ Mols/Hr}} \right) \times \left(\frac{\text{Total Mols/Hr}}{O_2 \text{ Mols/Hr}} \right)^{1/2}$$

Experimentally determined K_p values have been reported by Ross⁽¹⁾ and others. Table 1 lists calculated equilibrium conversions vs. temperature for various converter feed gas mixtures, and for these a curve of conversion vs. temperature is drawn.

Using a heat of reaction of 41,500 BTU/Lb Mol (@ 820°F) and enthalpy data⁽²⁾, the adiabatic ΔT 's at 100% conversion for various sulfur burning gas mixtures were calculated and listed in Table 2.

The reaction path may be determined as follows: After plotting the equilibrium conversion vs. temperature, a straight line is drawn originating at 0% conversion and 820°F (the feed conditions) and terminating at 100% conversion and 1,222°F (820°F plus 402°F of adiabatic temperature rise). Thus, the slope of the first catalytic stage "operating" line is set by the adiabatic ΔT . The horizontal lines represent interstage cooling of the reacting gas mixture. Since the mixture heat capacity remains almost constant throughout, the slopes of the operating lines for the following stages stay constant and the lines are parallel. Thus, the reaction path is conveniently determined in a graphical manner (Figure 1). Approaches to equilibrium are

(1) Ross L.W., Sulfur, 1966 No. 65, p. 37.

(2) Chemetron Corp., Physical and Thermodynamic Properties of Elements and Compounds, 1969.

FIGURE 1

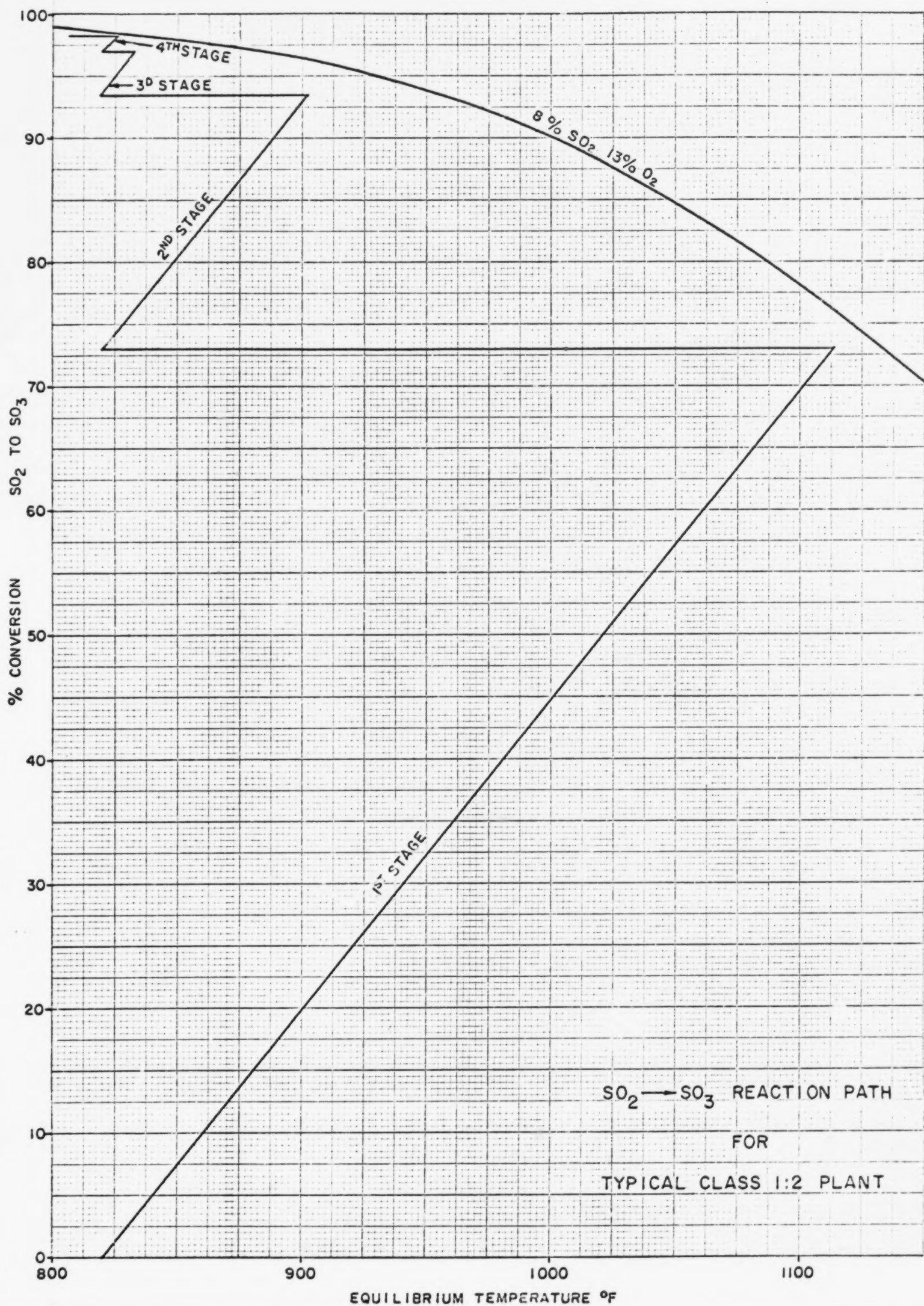


TABLE 1

EQUILIBRIUM CONVERSIONS



	4	5	6	7	8	9	10	11	12
Feed SO ₂ , Mol %	4	5	6	7	8	9	10	11	12
Feed O ₂ , Mol %	17	16	15	14	13	12	11	10	9
Conv., %									
					Temperature °F				
99.5	759.7	756.2	752.3	747.9	742.9	736.9	729.7	720.5	707.6
99.0	810.4	806.7	802.5	797.7	792.3	785.8	778.0	768.1	754.4
98.5	842.3	838.4	834.0	829.0	823.3	816.6	808.4	798.1	783.8
98.0	866.0	862.0	857.4	852.3	846.4	839.4	831.0	820.4	805.8
97.5	885.2	881.0	876.3	871.0	865.0	857.9	849.3	838.4	823.5
97.0	901.3	897.0	892.2	886.9	880.7	873.4	864.7	853.6	838.5
96.5	915.3	910.9	906.1	900.6	894.3	887.0	878.1	866.9	851.6
96.0	927.7	923.3	918.4	912.8	906.5	899.0	890.0	878.7	863.2
95.5	939.0	934.5	929.5	923.8	917.4	909.9	900.8	889.3	873.8
95.0	949.2	944.7	939.6	933.9	927.4	919.3	910.6	899.1	883.5
90.0	1,022.2	1,017.8	1,012.3	1,006.2	999.3	991.2	981.5	969.6	953.7
85.0	1,072.3	1,067.2	1,061.5	1,055.2	1,048.0	1,039.7	1,029.9	1,017.9	1,002.3
80.0	1,111.9	1,106.7	1,100.9	1,094.4	1,087.1	1,078.1	1,068.9	1,057.0	1,041.8
75.0	1,146.3	1,141.0	1,135.1	1,128.5	1,121.1	1,112.1	1,103.0	1,091.2	1,076.5
70.0	1,177.7	1,172.2	1,166.2	1,159.6	1,152.2	1,143.9	1,134.2	1,122.6	1,108.4
65.0	1,207.2	1,201.7	1,195.7	1,189.1	1,181.7	1,173.3	1,163.7	1,152.4	1,138.6
60.0	1,235.9	1,230.3	1,224.3	1,217.6	1,210.2	1,201.9	1,192.4	1,181.3	1,168.0
55.0	1,264.4	1,258.7	1,252.6	1,246.0	1,238.6	1,230.3	1,220.9	1,210.1	1,197.1
50.0	1,293.2	1,287.5	1,281.4	1,274.7	1,267.3	1,259.1	1,249.8	1,239.1	1,226.6
45.0	1,323.0	1,317.3	1,311.1	1,304.4	1,297.0	1,288.8	1,279.6	1,269.2	1,257.0

TABLE 2
ADIABATIC TEMPERATURE RISE
AT 100% CONVERSION

Feed SO ₂ Mol. %	4	5	6	7	8	9	10	11	12
Feed O ₂ Mol. %	17	16	15	14	13	12	11	10	9
Δ^T_{OF}	210	260	308	355	402	452	491	534	577

set at about 90% of the individual stage equilibrium conversion, depending on the catalyst activity and quantity and any limitation of maximum temperature imposed by the properties of the catalyst.

Figures 2a and 2b depict equilibrium conversion curves and the slopes of the adiabatic temperature rise for gas mixtures ranging from 4% to 12% SO₂ based on the air oxidation of sulfur.

Catalyst quantity requirements are determined by the reaction rate. For the SO₂ oxidation reaction a number of rate equations have been reported in the literature⁽¹⁾. At Chemico a computer simulation of the SO₂ converter is based upon the rate equation as proposed by Calderbank⁽²⁾. The fact that a number of different rate equations exist for the same reaction casts doubts upon the reliability of calculated catalyst quantity requirements. A discussion on the merits of one rate equation over another is outside the scope of this study; however, care has been taken to use calculated results wherever applicable on a relative basis.

(1) Honti G., Annales du Genie Chimique, International Sulfur Congress, Toulouse (1967), pp 206-214.

(2) Calderbank P.H., Chemical Engineering Progress, 49 (11), pp. 585-590.

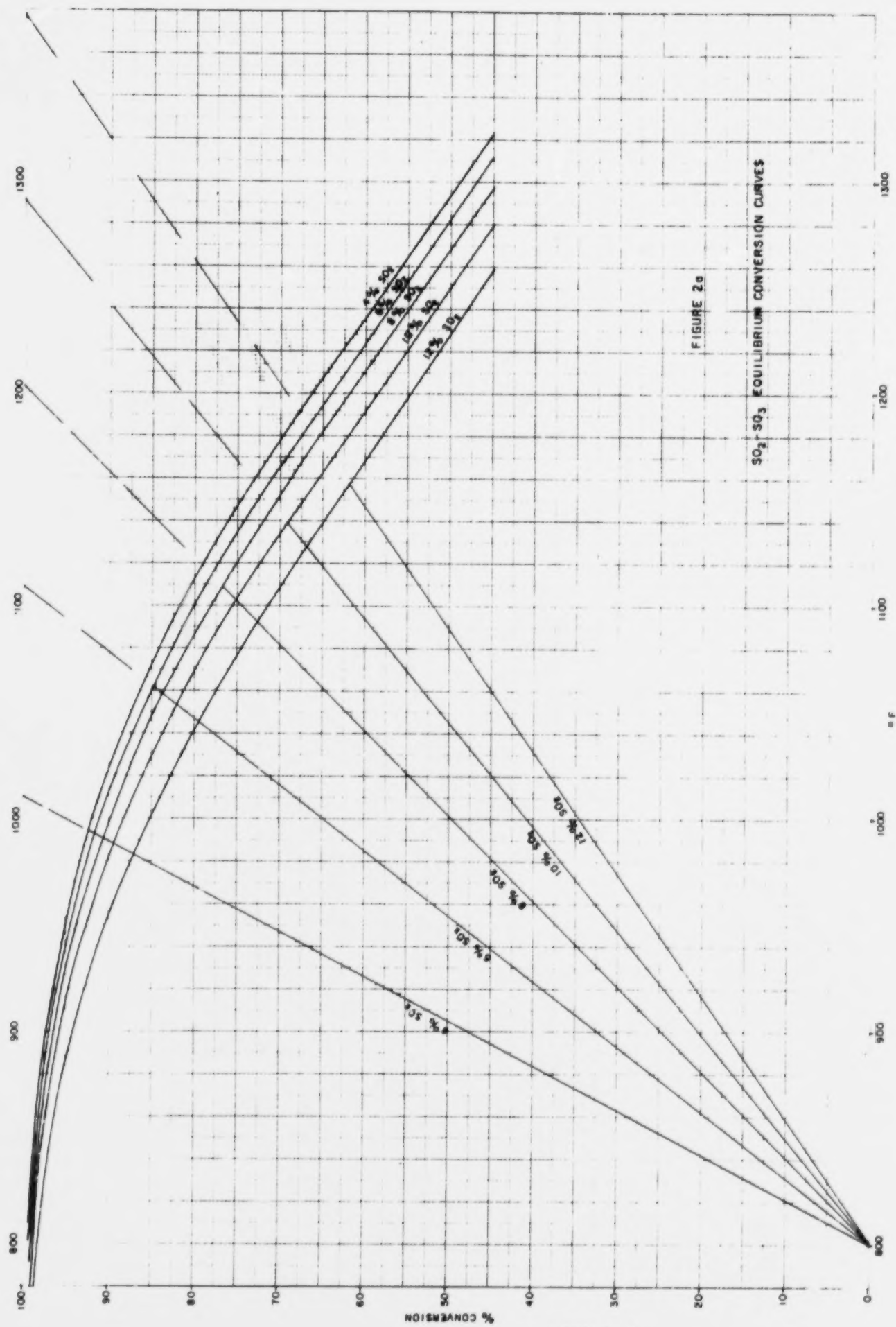


FIGURE 2a

SO_2 - SO_3 EQUILIBRIUM CONVERSION CURVES

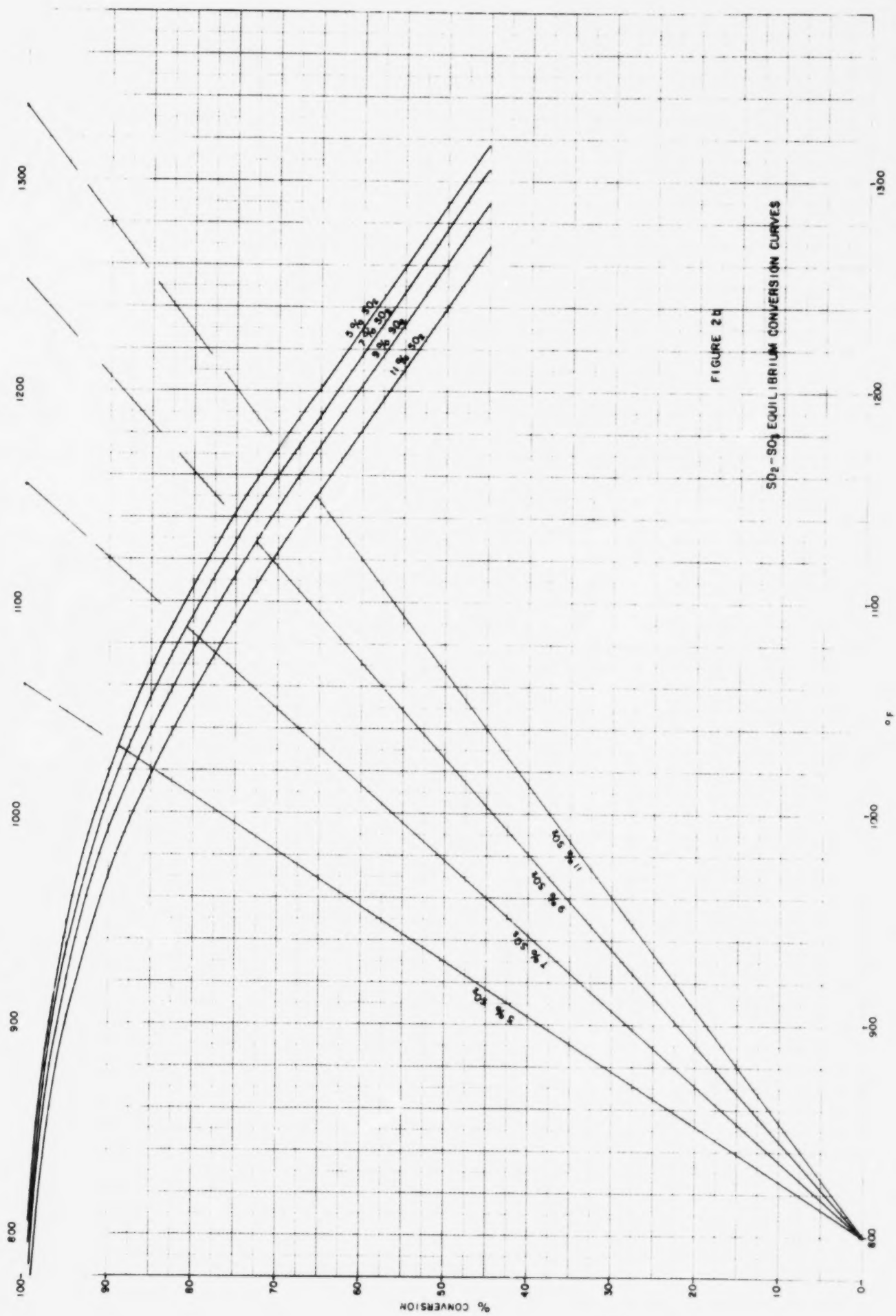


FIGURE 2b
 SO_2 - SO_3 EQUILIBRIUM CONVERSION CURVES

Ideal Stage Conversion Limits

Preceding any attempts to design or modify a converter system, the maximum conversion limits imposed by an ideal converter should be recognized. An ideal converter implies 100% approach to equilibrium conversion, in each stage and would require very large amounts of catalyst and/or infinite retention time. This discussion will be limited to three and four ideal stages of conversion which are the actual number of stages found in the majority of industrial converters.

Using the equilibrium conversion and adiabatic temperature rise data given in Figures 2 (a and b) the ideal reaction path was determined in the same manner as Figure 1, but continuing to the equilibrium, for sulfur burning gases ranging from 4% SO₂ to 12% SO₂, in all cases the N₂ content being 79%. This was done for four different types of ideal converters:

Type A

3 stages, all stage feed temperatures @ 820⁰F

Type B

3 stages, 820⁰F in @ stages 1 and 2, 770⁰F in
@ stage 3

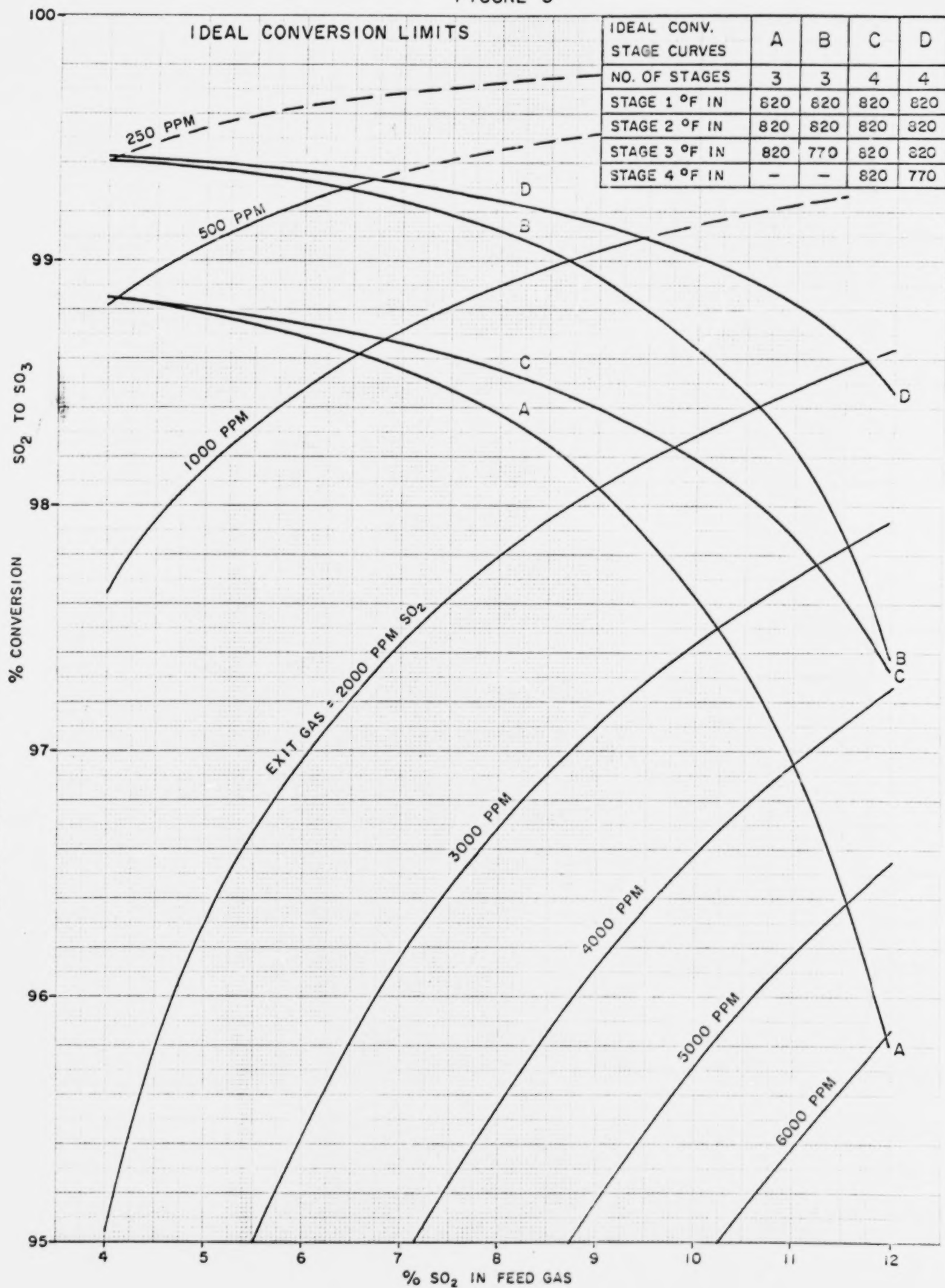
Type C

4 stages, 820⁰F in @ stages 1 to 4

Type D

4 stages, 820⁰F in @ stages 1 to 3, 770⁰F in
@ stage 4

FIGURE 3



The ideal conversion obtained was plotted on Figure 3, where curves A, B, C and D represent the types of converter. The coordinates are percentage conversion of SO_2 and percent SO_2 in the reactor feed gas. To expand the scope of Figure 3, curves of equal concentration of SO_2 in the plant tail gas (ppm SO_2) were superimposed. For example, for an 8% SO_2 using a 4 stage low temperature converter (D) the maximum conversion is 99.24% and the exit SO_2 ppm is about 600.

The significance of Figure 3 is that it shows what can be done in any converter system within the limitations imposed by operating conditions. This will be discussed further in Part IV-C. The lowering of stage feed temperature from 820^oF to 770^oF was done only for the last stage because there would not be any significant conversion improvement if the feed temperature was lowered for all the stages, and, from a heat exchange view point, the last stage is the most practical place to lower feed temperatures in an existing plant. 770^oF is purely an arbitrary temperature, in the actual case lower feed temperatures would be chosen according to catalyst considerations.

It should be restressed that Figure 3 represents maximum conversions under ideal conditions.

The Variation of Conversion Efficiency with Plant Capacity

Many sulfuric units are operated under process conditions other than design in order to increase plant capacity. In sulfur burning plants burning more sulfur without increasing air flow results in a higher concentration SO_2 gas mixture out of the sulfur furnace, the $\text{O}_2:\text{SO}_2$ ratio is decreased and the net result is a reduction of the SO_2

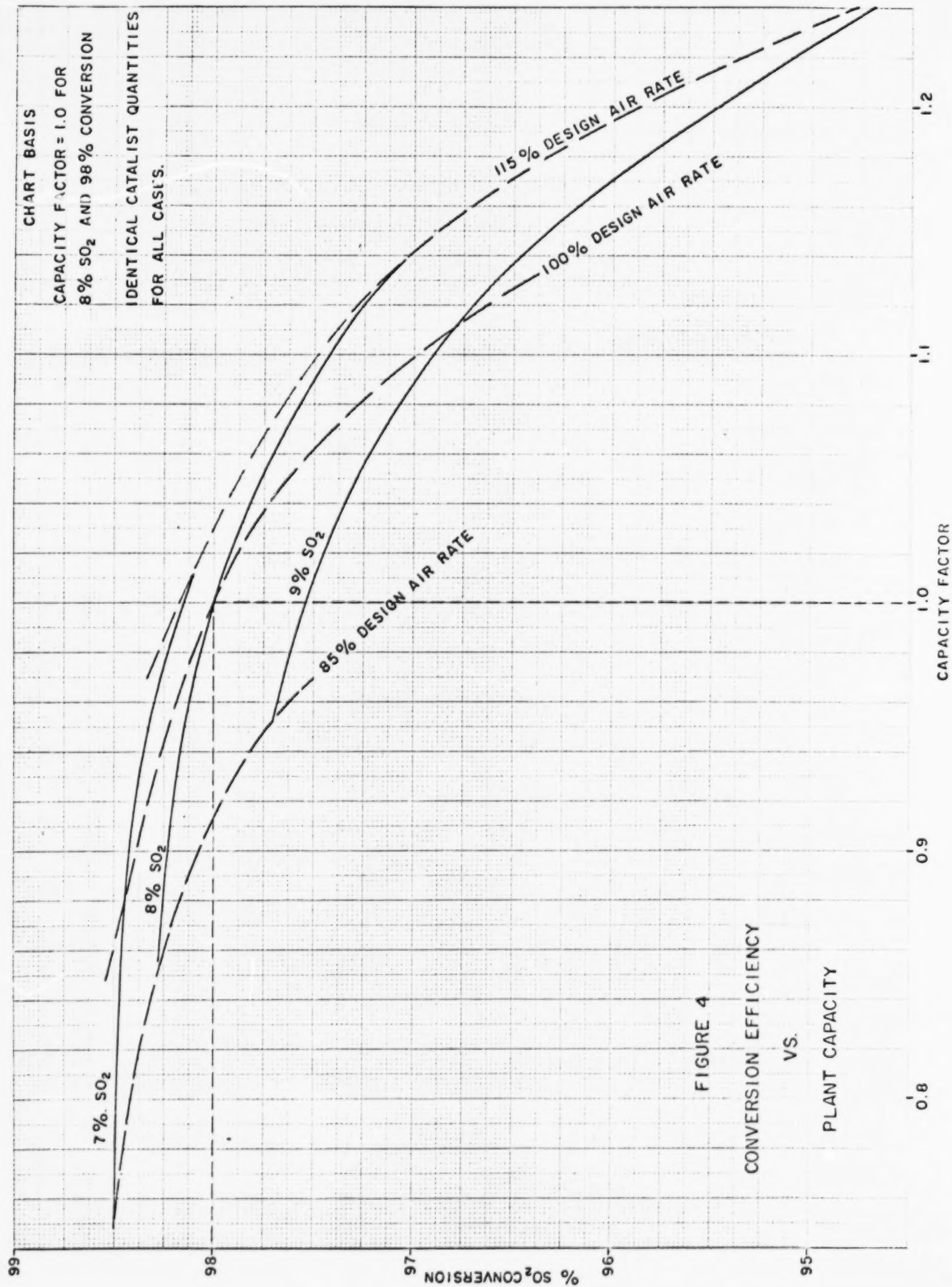
conversion efficiency thus increasing SO_2 emission levels. If blower capacity permits, increased production may also be obtained without reducing the $\text{O}_2:\text{SO}_2$ ratio by increasing air flow at the same time as the sulfur.

The possible effects were determined for a standard sulfur burning plant. A capacity factor of 1.0 was assigned to operation at the following design characteristics:

- 8% SO_2 sulfur burning
- 4 stage converter
- SO_2 conversions after the four catalytic stages set at 72%, 93%, 96.8% and 98%
- 820°F feed temperature at all the stages
- A main blower with 15% over capacity

Using the Chemico converter simulation program, catalyst quantities were calculated for each stage of the above converter. The run was repeated for feed SO_2 concentrations of 7% and 9% using the same amount of catalyst. Thus, the effect of just varying the feed sulfur was determined, everything else being constant. The calculation was repeated at each SO_2 concentration for maximum and minimum air rates, these being 115% and 85% respectively of the design air rate. The data was plotted on Figure 4.

From the plot of Figure 4 it is readily seen that conversion is a function of plant throughput and feed SO_2 concentration. For example, the conversion of an 8% SO_2 gas can be improved from 98 to about 98.28% by reducing plant throughput alone, the respective capacity



factors being 1.0 and 0.852. However, if less sulfur is burned at constant throughput such as the 7% SO_2 at 100% design air rate level, the conversion is 98.44% and the capacity 0.879. This indicates that at least for the given example, decreasing SO_2 concentration is a better means of control. The example is shown in Table 3.

Figure 4 applies only to sulfur burning plants. Wet gas plants are less predictable due to the greater variety of feed gas concentrations encountered, but the same principle applies.

Sulfuric Acid Mist

Sulfuric acid mist consists of small drops of sulfuric acid, usually over 90% concentration, formed in the vapor phase from water vapor and SO_3 . Once formed it is extremely stable and is not readily separated or absorbed. It is this stability that is of importance in sulfuric acid plants and designs of these plants would be different if it were not for the peculiar properties of this mist.

In sulfur based acid plants dry sulfur is burned in dry air and water vapor is kept out of the plant. In wet gas plants, where the formation of mist is inevitable in the wet purification section (as almost all SO_2 bearing gases will contain traces of SO_3) this mist is removed by electrostatic precipitators or special filters and the gas dried before any further SO_3 is formed. Only in the comparatively few plants, usually based on H_2S , where the undried gas is reacted in the converter, is mist formation deliberately permitted and in these plants there is always special treatment of the tail gas to remove the mist.

TABLE 3

EMISSION CONTROL
BY REDUCING PRODUCTION

	<u>Base Case</u>	<u>Reduced Throughput</u>	<u>Reduced SO₂ Content</u>
% SO ₂ in Feed	8	8	7
Air Rate, % of Design	100	85	100
% Conversion	98.00	98.28	98.44
Capacity Factor	1.0	0.852	0.879
Exit ppm SO ₂	1,813	1,560	1,232

In spite of the precautions taken, some mist formation does take place in most plants. This may result from the inadequate performance of the drying tower or moisture in the sulfur, but the most common cause is the presence of hydrocarbons in the sulfur which burn with it producing water which will combine with the SO_3 as the gas cools in the economizer or absorption tower. This mist formation may be accentuated by sudden chilling of the gas on cold surfaces, an effect sometimes produced by rain on the gas duct. Such information as exists indicates this type of mist consists of sulfuric acid drops of between 1 and 5 microns.

A most persistent form of this mist is produced in most oleum plants. In these plants, oleum (i. e. sulfuric acid containing excess SO_3 in solution) is produced in an preliminary absorption step before the main absorption tower. Only part of the SO_3 is absorbed and the gas leaving the oleum tower still contains SO_3 , and this is absorbed in the absorption tower. In spite of this preliminary absorption, the stack gas is always much more misty than when the oleum tower is bypassed. The mechanism of this mist formation is not clearly understood but it has been established that it is formed in the final absorption tower, not in the oleum tower. The important fact from a pollution standpoint is that this mist consists of very much finer (0.2-3.0 micron) particles than that present in the normal mist produced in plants where oleum is not a product.

For plants producing 98% acid it has been reported⁽¹⁾ that about 30% by weight of the particles are smaller than 2 microns, while for oleum plants 85-95% by weight of particles are smaller than 2 microns.

(1) E. P. Stastny, "Electrostatic Precipitation" - Chemical Engineering Progress, Vol. 62, No. 4 - April 1966

Another cause of mist formation is the presence of nitrogen oxides in the converted gas. This may result from the fixation of atmospheric nitrogen in high temperature furnaces and the slightly misty stack of sulfur burning plants was at one time thought to arise from this cause.

More commonly nitrogen oxides will result from nitrogen compounds in the raw material used, spent acids from organic reaction being most likely to produce them. Formation of nitrogen oxides can be avoided by choosing the correct operating conditions for the reactor (decomposition furnace, roaster, etc.) in which they are formed. For instance, in the decomposition of spent acid containing nitrogen compounds, operation of the furnace at about 2,000⁰ F and a low oxygen content will ensure the decomposition products do not contain more than 100 ppm of nitrogen oxides.

Again, the exact mechanism of mist formation is something of a mystery but it may result from the oxidation of residual SO₂ by nitrogen oxides (the chamber plant reactions) in the stack itself and in this case the only satisfactory solution is to prevent the nitrogen oxide formation.

Several methods of removing mist are described elsewhere in the report. Knitted mesh filters are the most commonly used (taking a pressure drop of 2-3" W.G.) and are satisfactory for all but the very fine mist from oleum plants. In this case, the packed glass wool filter with a much higher pressure drop (12" - 18" W.G.) is necessary, as here we are dealing with mist particles in the 0.2 to 2.0 micron range. Electrostatic mist preceipitators will remove almost all mists with a pressure drop of <1" W.G. if properly chosen. Packed scrubbers will have little effect on removing mist. High pressure drop (35"-40" W.G.) venturi scrubbers will remove all but the finer mist particles.

Acid Mist, SO_3 and H_2SO_4 Vapor

In a discussion of acid mist it is important to distinguish between it, gaseous SO_3 and sulfuric acid vapor.

At the temperatures in an acid plant SO_3 is a colorless gas and, therefore, invisible. If present in the stack gas of an acid plant, as a result of poor absorber operation, it will combine with water vapor in the atmosphere when it leaves the stack and become a visible mist. The only way of preventing this mist formation is to ensure that the SO_3 content of the gas leaving the absorber is very low, by proper design and operation of the tower.

The stack gas leaving the absorption tower will always contain sulfuric acid vapor as it will be in substantial equilibrium with the absorber acid. The only way this can be reduced is by cooling, and it may, in fact, condense in long ducts to the stack or in the stack itself, sometimes being carried out of the stack as relatively large droplets which fall in the vicinity of the plant. As operation of the absorption tower at low temperatures may make good absorption more difficult to achieve, it is clearly necessary to strike a proper balance between a high SO_3 content on the one hand and a high acid vapor content on the other.

B. CLASSIFICATION OF SULFURIC ACID PLANTS

For purposes of the study sulfuric acid plants have been divided into groups which tend to have the same types of emission problems, and consequently, the same types of remedies will be applicable to most plants in any one classification. Consideration is also given to production cost which is utilized in Part V.

These classifications have been designated for existing plants:

- 1.0 for chamber acid plants
- 1.1 for sulfur burning contact plants with 3 conversion stages
- 1.2 for sulfur burning contact plants with 4 conversion stages
- 1.3 for "wet gas" contact plants with 3 conversion stages
- 1.4 for "wet gas" contact plants with 4 conversion stages
- 1.5 for sulfuric acid concentrators

Each classification and its characteristics are more fully described in the next few pages.

In order to determine the approximate number of plants in each classification it was assumed that plants built through 1960 were 3 stage plants and those built after 1960 were 4 stage plants. Although this is an arbitrary division, 1960 was the time when the 4 stage conversion plant came into general use in the United States and conversion was increased from 96% to 98%.

Plant Classification 1.0

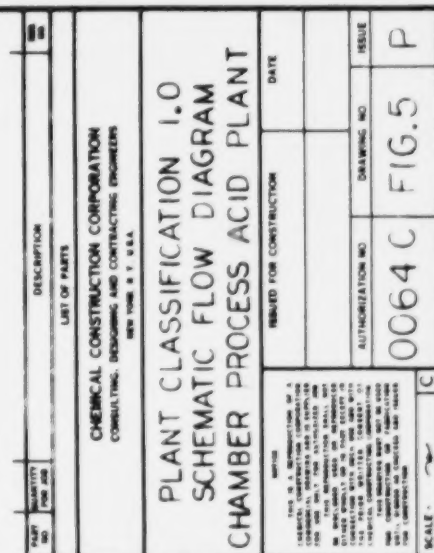
Chamber type acid plants, though they are gradually disappearing, are included in a separate classification because their emissions are quite different from the contact process plant. Most chamber plants are of small capacity, ranging from 40 to a little over 100 short tons per day of 100% H_2SO_4 equivalent. The chamber process produces acid of about 78% which finds little use outside of acidulation of phosphate rock to produce single superphosphate fertilizers. Most chamber plants are located in the southeastern states, as are most of the large contact plants which supply acid for production of more complex phosphatic fertilizers.

Tail gas emissions from chamber plants are approximately as follows:-

Flow Rate	100-160 MSCF/ton of acid (as 100% H_2SO_4)
SO_2 Content	1,500-4,000 ppm
Acid Mist Content	5-50 mg/SCF
NO_2 Content	1,000 ppm
NO Content	500 ppm

The chamber process is illustrated by Figure 5.

Presently operating chamber plants burn sulfur as raw material. There are fewer than 40 remaining in the United States.

[illegible]

Plant Classification 1.1

This classification, illustrated by Figure 6, includes sulfur burning contact plants having three conversion stages. These plants, for the most part built prior to 1960 in the United States, may produce various grades of acid from 93% H_2SO_4 to oleum, or combinations thereof.

Typical operating characteristics of these plants are as follows when operating at design conditions:-

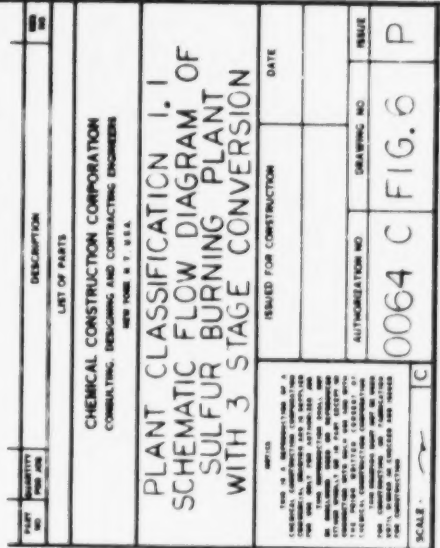
SO_2 in Converter Feed	7.5 to 8.5 Mol %
Conversion of SO_2 to SO_3	95 to 96%

Characteristics of the tail gas emission from these plants at design conditions are as follows:-

Maximum Flow *	91,800 SCF per ton of acid (as 100% H_2SO_4)
SO_2 Content	3,000 to 5,000 ppm
Acid Mist	2 to 20 mg/SCF
SO_3 Content	0.3 to 1.3 ppm **
Oxygen	9 to 11% by volume
Water	Nil
Inert Gas (N_2 , A, CO_2 , etc)	Remainder
Temperature	150-180°F

* Under any combination of SO_2 strength in the converter feed gas and conversion efficiency from the operating characteristics shown above. This would be a normal design condition for a tail gas scrubber.

** Calculated from vapor pressure of SO_3 over 98.5% H_2SO_4 for given temperature range.



1. 姓名	2. 性别	3. 年龄	4. 民族	5. 籍贯	6. 职业	7. 学历	8. 婚姻状况	9. 健康状况	10. 其他
11. 身份证号	12. 联系电话	13. 电子邮箱	14. 联系地址	15. 联系地址	16. 联系地址	17. 联系地址	18. 联系地址	19. 联系地址	20. 联系地址

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Sulfur losses per ton of acid produced (as 100% H_2SO_4) are as follows at design conditions:-

	<u>Tons of Sulfur</u>
as SO_2	0.014 to 0.017
as Mist when producing 99% acid	0.002 maximum
as Mist when producing oleums	0.005 maximum

These plants were in many cases capable of producing acid at rates significantly higher than design but at lower efficiency and with consequently greater sulfur losses. This is due to design factors included in the plant designs which would permit operation at higher capacities. Often plants were designed to produce as much as 50% excess capacity at a lower conversion efficiency, and with excess pressure capability in the blower and additional catalyst space in the converter to permit reaching either design capacity with dirty catalyst or higher capacity by addition of catalyst.

This type of plant can take maximum advantage of either a tail gas recovery process which returns recovered SO_2 to the plant, or an add-on dual absorption process, by operating at maximum production rate and still keeping emissions within reasonable limitations after inclusion of a control system.

Many older plants are congested and surrounded by other facilities which may make addition of new equipment for emission control very difficult.

Sulfur burning plants always have sufficient heat to produce steam in excess of plant requirements for heating and mechanical drives. The use of steam generated is usually dictated by adjacent facilities. If the acid plant is associated with a wet process phosphoric acid plant, much of the steam can be utilized on the concentration of phosphoric acid. If the acid plant is associated with a refinery or other process plant, excess steam can usually be used in the appropriate steam header. In the case where excess steam has no user available, driving a turbo generator can reduce plant power requirements.

In calculations of control costs it has been assumed, to be consistent, that essentially all steam is exported and all drives are electric.

The oleum system, shown dotted in Figure 6, is included only in plants producing oleum grades. The production of oleum affects only the acid mist emission from the plant, mist from oleum plants being more finely divided than that from plants producing acid grades at less than 99%, and requiring a different type of mist control device for such a plant for effective control. In instances where separate devices or systems are incorporated for SO_2 control and for mist control, the mist control systems for acid and oleum plants will be different. Tail gas treatment systems which control both mist and SO_2 would be less affected by the grades of products produced.

Operating United States plants falling within this classification vary in capacity from 50 tons per day to 4,000 tons per day; however, no single unit in these plants exceeds about 750 tons per day.

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There are about 60 plants in this category producing over 7,500,000 T/Y of acid with no oleum. The majority of these plants are located in the gulf coast states and the middle west.

About 35 additional plants produce over 4,000,000 additional T/Y of acid, including some oleum. Many of these plants are located in the northeast and midwest within AQCRs.

Plant Classification 1.2

This type plant, illustrated by Figure 7, is a typical modern 4-stage conversion sulfur burning acid plant representative of those built from 1960 to the present. These plants may produce a variety of acid grades ranging from 93% H_2SO_4 to various oleum grades, or combinations thereof.

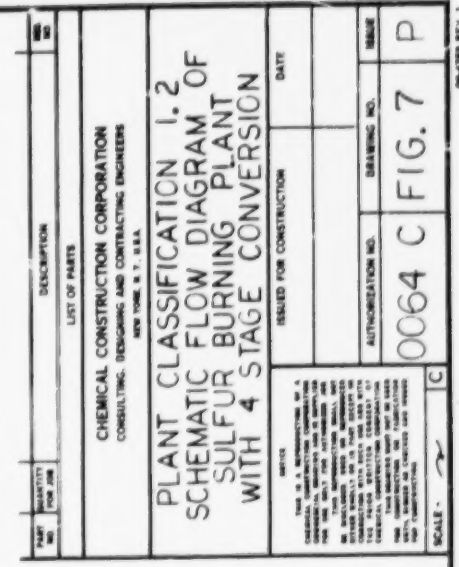
Typical operating characteristics of these plants are as follows when operating at design conditions:-

SO_2 in converter feed	7.5 to 8.5 Mol %
Conversion of SO_2 to SO_3	96 to 98%

Characteristics of the tail gas emission from these plants at design conditions are as follows:-

Maximum Rate*	90,800 SCF per ton of acid (as 100% H_2SO_4)
SO_2 Content	1,500 to 4,000 ppm
Acid Mist	2 to 20 mg/SCF
SO_3 Content	0.3-1.3 ppm
Oxygen	9-11% by Volume
Water	Nil
Inert Gas (N_2 , A, CO_2 , etc)	Remainder
Temperature	150° - 180°F

- * Under any combination of SO_2 strength in the converter feed gas and conversion efficiency from the operating characteristics shown above.

[illegible]

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Sulfur losses per ton of acid produced (as 100% H_2SO_4) are as follows at design conditions:

	<u>Tons of Sulfur</u>
As SO_2	0.007 to 0.014
As Mist when producing 99% acid	0.002 maximum
As Mist when producing oleum	0.005 maximum

The majority of these plants are probably being operated at or near their design capacities today, and the newest and largest at 98% conversion.

Comments with respect to steam production and optional oleum producing facilities included with the description of class 1.1 apply equally to class 1.2.

Operating U.S. plants in classification 1.2 generally have a capacity of 250 T/D or more. The largest plants do not exceed 2,000 tons per day in a single train, though some plants have multiple units. It is beyond this point where structural problems apparently outweigh the cost advantage of a single train plant, using the conventional low pressure process. There are over 40 plants of classification 1.2 which produce over 11,000,000 tons annually of acid. The majority are located in the southeastern states outside of AQCRs. Approximately 10% are oleum producers.

A number of plants are designed for additional capacity at reduced efficiency with provisions for additional catalyst. These plants could improve conversion rate and reduce sulfur emission by

addition of catalyst while continuing to operate at the basic design rate, although the conversion improvement is limited, as shown in Part III A. These plants are technically suited to add-on dual absorption or tail gas recovery systems of most types. Most were originally built with some form of mist control device to reduce the acid mist in the tail gas, and the 2 mg/SCF mist level in the tail gas reflects plants so equipped. The class 1.2 plants are not likely to be as cramped for space required for an emission control system as other class 1.1 plants, although this remains a distinct problem. Finding space for an additional 28' diameter absorber and 35' diameter converter with attendant duct work and heat exchangers such as would be required for a large plant will not be simple. From Part V it can be seen that tail gas recovery processes are more attractive for larger plants such as are encountered in class 1.2.

Plant Classification 1.3

Figure 8 illustrates schematically a typical "wet gas" sulfuric acid plant with 3 stage conversion of the type included in classification 1.3. These 3 stage plants were mostly built before 1960, and may produce various grades of acid from 93% H_2SO_4 to oleum using a variety of sulfur sources, singularly or in combination. Sulfur sources include SO_2 resulting from roasting of various copper, zinc and other ore concentrates, burning of spent alkylation acid or H_2S from refinery operations, roasting of iron pyrites, recovery of SO_2 from copper converter and reverberatory furnace flues, and a few others.

While these plants differ widely from each other in detail, they all lend themselves to similar methods of emission control. All generally require similar types of in-plant control systems, but different from those suitable for sulfur burning plants, as well as generally larger add-on systems for a given plant capacity because of the normally larger quantities of gas to be handled and sulfur values to be recovered.

Typical operating characteristics of these plants when operating at design conditions are given below for various feedstock:-

<u>Feedstock</u>	<u>SO_2 in Converter Feed - Mol %</u>	<u>Conversion SO_2 to SO_3 %</u>
H_2S	7	94 to 96
Pyrites	6.5 to 7.5	94 to 96
Acid Sludge	6 to 8	94 to 96
Copper Converter Gas	3 to 7	90 to 95
Roaster Gas	5 to 7	94 to 96

Characteristics of the tail gas emissions from these plants may be expected to fall in the following ranges:-

Feedstock	Maximum Rate SCF/ton of Acid (as 100% H_2SO_4)	SO ₂ Content, ppm	Acid Mist mg/SCF	
			Producing 99% Acid	Producing Oleum
H ₂ S	100,000	3,000 to 5,000	2 to 20	5 to 50
Pyrites	109,000	2,500 to 5,000	2 to 20	5 to 50
Acid Sludge	119,000	2,500 to 4,000	2 to 20	5 to 50
Copper Converter Gas	192,000	2,000 to 10,000	2 to 20	5 to 50
Roaster Gas	145,000	2,000 to 5,000	2 to 20	5 to 50

* Under any combination of SO₂ strength in the converter feed gas and conversion efficiency from the operating characteristics shown above. The high mist rates are encountered in plants with no control devices.

With this type of plant the variation in the other components in the tail gas varies so widely that any compositions given would be meaningless.

Sulfur losses per ton of acid produced (as 100% H_2SO_4) are as follows at design conditions:-

Feedstock	Sulfur Loss, Tons		
	As SO ₂	As Acid Mist	
		Producing 99% Acid	Producing Oleum
H ₂ S	0.014 to 0.021	.002 max.	.006 max.
Pyrites	0.014 to 0.021	.002 max.	.006 max.
Acid Sludge	0.014 to 0.021	.003 max.	.007 max.
Copper Converter Gas	0.017 to 0.036	.004 max.	.011 max.
Roaster Gas	0.014 to 0.021	.003 max.	.008 max.

Plants based on pyrites, H_2S , or acid sludge (spent acid) will have excess heat available for steam production and in most cases will, in fact, include waste heat boilers. Plants based on roaster or smelter gases from metallurgical processes are not normally steam producers. The steam produced may be used in the plant for driving the main blower and occasionally for driving the blowers and pumps.

The steam system adopted on any plant will depend on factors outside the acid plant. Thus, where an acid plant is part of a phosphoric acid production unit, it will be found best to drive the blower with a back pressure turbine and so provide low pressure steam for phosphoric acid evaporation.

As with classification 1.1 and 1.2, economics have been calculated on the basis of all electric drives for plant equipment, with a nominal credit for steam generated. This has been done for comparison purposes.

Oleum facilities are optional, and the comments made for classification 1.1 apply to classification 1.3 as well.

Many plants of this type operate on combinations of feed stocks and include sulfur as well as one or more of the feedstocks mentioned above. These plants require that the gas be cooled and cleaned before introduction into the converter system.

Except in the case of plants based on copper converter gas, most methods of emission control can be applied. The cyclical nature of

copper converter operation makes the application of the dual absorption process, or even careful converter control much more difficult.

Many plants of this type are located in congested metallurgical complexes and systems with minimum space requirements may be preferred.

Those locations with several units close together recovering acid from smelters may favorably utilize several tail gas scrubbing units feeding to a single recovery system.

Operating United States plants of this type range in size from about 100 to 1,000 ST/D capacity. Nearly 60 plants produce about 7,500,000 tons of acid annually. About 40% of these plants produce some oleum, with most oleum producers being sludge burning operations. Locations are scattered, with concentrations in petroleum refining areas of California, Texas and Chicago. Others are scattered, principally in mining areas of the western states and outside of AQCRs.

Plant Classification 1.4

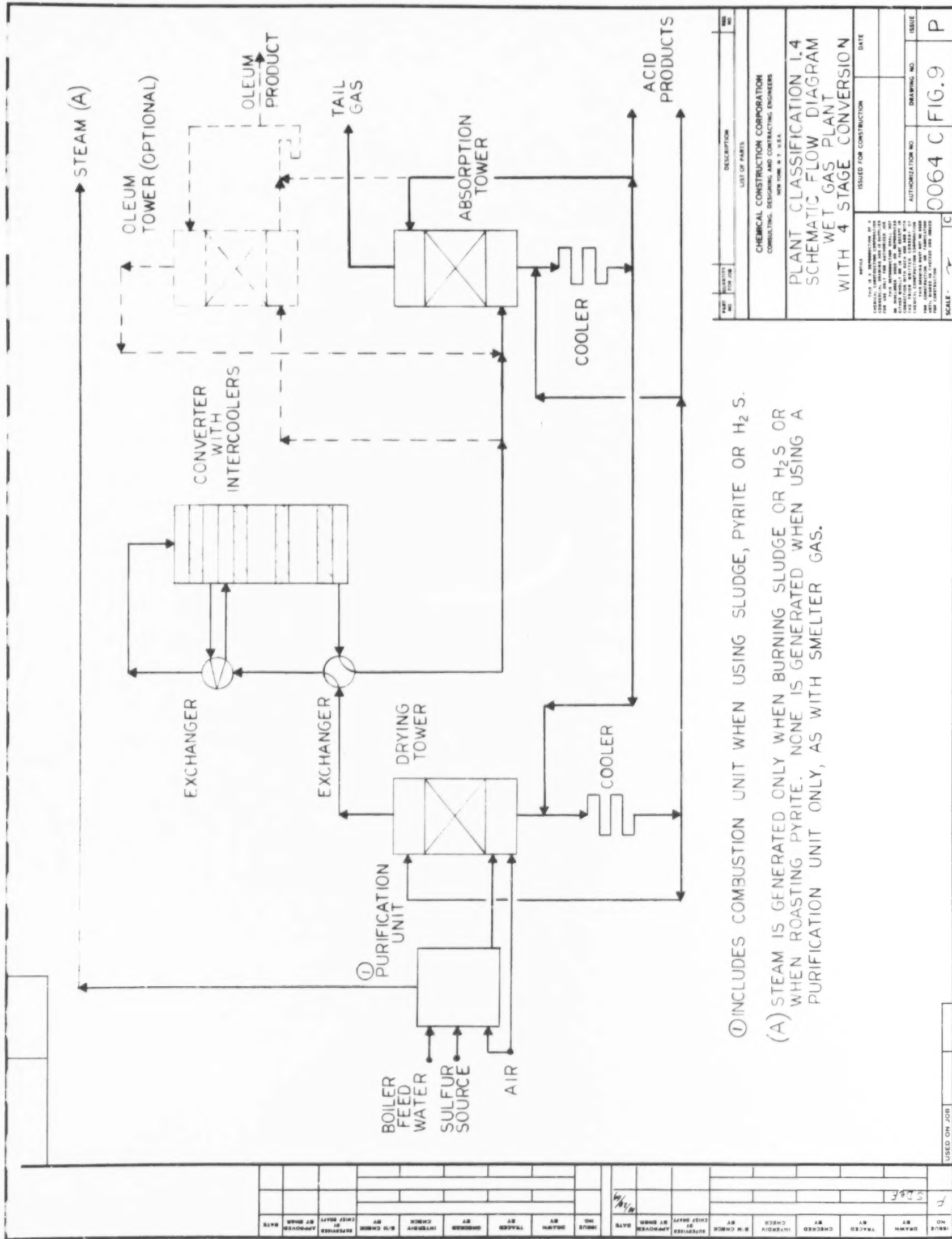
This classification illustrated by figure 9, includes typical modern "wet gas" sulfuric acid plants having 4 stages of conversion, typical of plants built in the sixties. As with other classifications, these plants produce a variety of product grades ranging from 93% acid through oleum, and combinations of these products. Sulfur is derived from the same variety of sources as described in classification 1.3.

While these plants differ widely from each other in detail, they all lend themselves to similar methods of emission control. All generally require similar types of in plant control systems, but different from those suitable for sulfur burning plants, as well as generally larger add-on systems for a given plant capacity because of the normally larger quantities of gas to be handled and sulfur quantities to be recovered.

Typical operating characteristics of these plants when operating at design conditions are given below for various feedstocks:-

<u>Feedstock</u>	<u>SO₂ in Converter</u>		<u>Conversion</u>
	<u>Feed, Mol %</u>		<u>SO₂ to SO₃, %</u>
H ₂ S	6.5	to 7.5	95 to 98
Pyrites	6.5	to 7.5	95 to 98
Acid Sludge	6	to 8	95 to 98
Copper Converter Gas	3	to 7	94 to 98
Roaster Gas	5	to 7	95 to 98

Characteristics of the tail gas emissions from these plants may be expected to fall in the following ranges: -



REVISIONS		DESCRIPTION	
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LIST OF PARTS			
CHEMICAL CONSTRUCTION CORPORATION CONSULTING, DESIGNING AND CONTRACTING ENGINEERS NEW YORK, N. Y. U.S.A.			
PLANT CLASSIFICATION I.4 SCHEMATIC FLOW DIAGRAM WET GAS PLANT WITH 4 STAGE CONVERSION			
ISSUED FOR CONSTRUCTION		DATE	
AUTHORIZATION NO.		DRAWING NO.	
0064 C		FIG. 9	
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SCALE: 1" = 10'			

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<u>Feedstock</u>	Maximum Rate [*] SCF/ton of Acid (as 100% H ₂ SO ₄)	SO ₂ Content, ppm	Acid Mist Mg/SCF	
			Producing	Producing
			99% Acid	Oleum
H ₂ S	99,000	1,500 to 4,000	2 to 20	5 to 50
Pyrites	108,000	1,500 to 4,000	2 to 20	5 to 50
Acid Sludge	117,500	1,500 to 5,000	2 to 20	5 to 50
Copper Converter				
Gas	184,000	2,000 to 7,000	2 to 20	5 to 50
Roaster Gas	143,000	1,000 to 4,000	2 to 20	5 to 50

* Under any combination of SO₂ strength in the converter feed gas and conversion efficiency taken from the operating characteristics shown on the preceeding page. The higher mist rates are those that would be encountered on plants with no mist control device.

Sulfur losses per ton of acid produced (as 100% H₂SO₄) are as follows at design conditions:-

<u>Feedstock</u>	Sulfur Loss, Tons		
	As SO ₂	As Acid Mist	
		Producing 99% Acid	Producing Oleum
H ₂ S	0.007 to 0.017	.002 max.	.005 max.
Pyrites	0.007 to 0.017	.002 max.	.006 max.
Acid Sludge	0.007 to 0.017	.003 max.	.006 max.
Copper Converter Gas	0.014 to 0.021	.004 max.	.010 max.
Roaster Gas	0.007 to 0.017	.003 max.	.008 max.

The comments regarding steam, oleum production, and economic calculations for classification 1.3 apply equally to class 1.4.

Many plants of this type operate on combinations of feed stocks, including sulfur as well as one or more of the feedstocks mentioned above. These

plants require that the gas be cooled and cleaned before introduction into the converter system. Within the same limitations as class 1.3 most emission control methods may be applied including the addition of a second absorption stage, addition of catalyst as with classification 1.2, plus recovery processes which remove SO_2 , SO_3 and acid mist from tail gases. Locations with smelter operations having several units or with other emission sources may find advantage in using several individual tail gas scrubbers contributing recovered sulfur compounds to a central recovery system.

Plants in this classification range in capacity from about 150 T/D to 1,600 T/D. These plants are relatively few, numbering about 20, but produce about 4,000,000 tons of acid annually. Most are connected with mining operations scattered in the western states. Several are connected with refinery operations on the Louisiana-Texas gulf coast. About 1/3 are oleum producers.

Plant Classification 1.5

Two major types of sulfuric acid concentrators are in use:

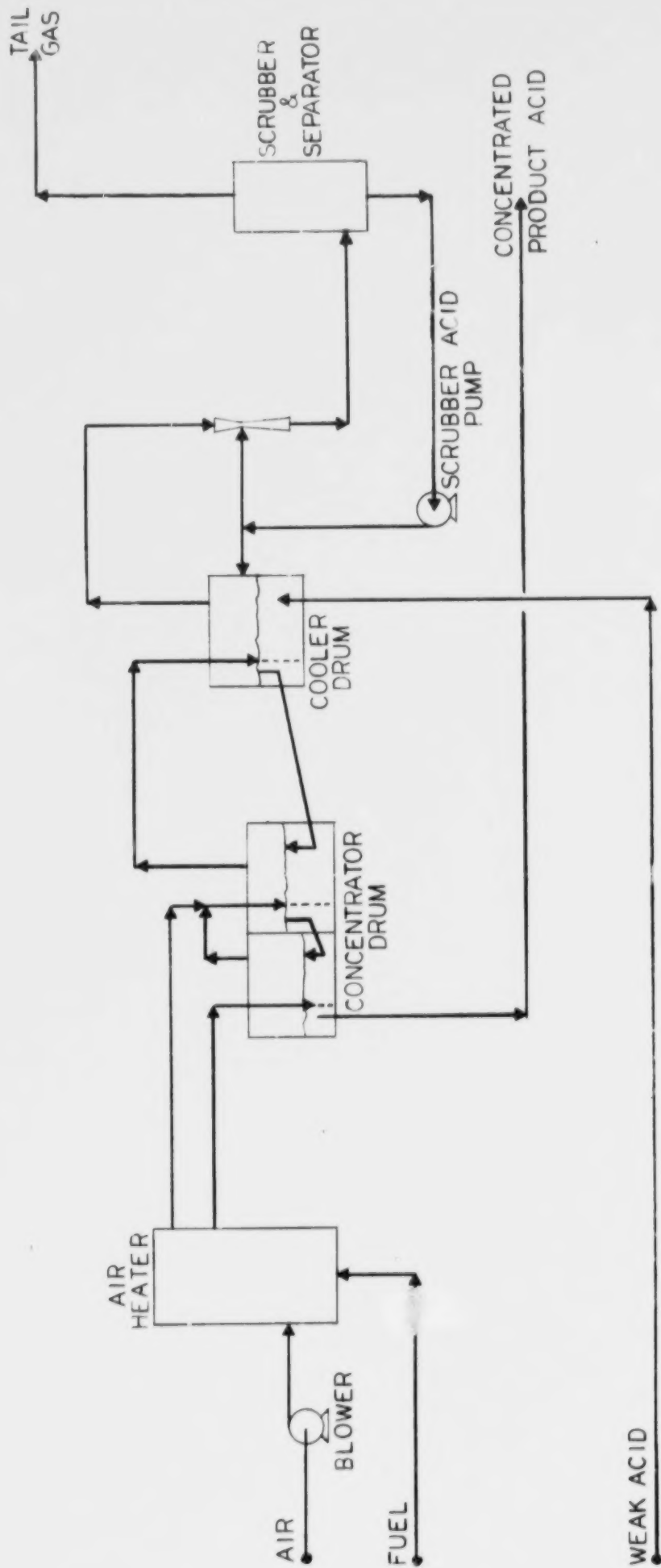
Indirectly Heated Under Vacuum:

Operating under high vacuums water is evaporated via heating the dilute spent acid in steam heated exchangers, the hot acid is discharged into a flash chamber where flash evaporation takes place and the overhead vapors consisting of water and some H_2SO_4 are liquified in a condenser. This type of operation does not have gaseous emission problems (Mantius type). The condenser water may be slightly acidic.

Directly Heated Drum Concentrators:

This is a popular unit for large capacities and high concentrations (illustrated by Figure 10). Counter-current contact of a hot gas mixture and the weak acid in three separate drums which represent stages of contact provides direct contact heating to evaporate water. H_2SO_4 vapor formed in the high concentration stage is partly condensed in the following stages. Prior to being discharged to the atmosphere the tail gas is treated for final mist removal in a venturi scrubber; many earlier plants used electrostatic mist eliminators for this purpose.

When operated under design conditions the H_2SO_4 mist emission should not exceed 5 mgs H_2SO_4 /SCF, above which level a visible plume persists. Mist emissions as high as 40-50 mgs/SCF have been reported in the past, however, these have probably been from war time



PART NO.	QUANTITY FOR JOB	DESCRIPTION
LIST OF PARTS		
CHEMICAL CONSTRUCTION CORPORATION CONSULTING, DESIGNING AND CONTRACTING ENGINEERS NEW YORK, N. Y. U.S.A.		
PLANT CLASSIFICATION I.5 SCHEMATIC FLOW DIAGRAM SULFURIC ACID CONCENTRATOR		
ISSUED FOR CONSTRUCTION		DATE
AUTHORIZATION NO.	DRAWING NO.	ISSUE
0064C	FIG.10	P
SCALE - 1" = 10'		10

ordnance works which very likely were operating under overload conditions with malfunctioning electrostatic mist separators.

Stack gas H_2SO_4 mist loading is a function of:-

- . collection efficiency of venturi scrubber
- . high stage drum vapor pressure
- . air rate through the high stage
- . liquid entrainment from cooler drum

The main function of concentrators is to remove water, and the exit gases contain large quantities of water vapor which, under certain weather conditions, condense to form a visible fog. When concentrating nitration spent acid, impurities in the form of nitric and nitrous acids, toluene and nitrobenzenes may be introduced into the concentrator and distilled in the cooler drum resulting with a redish brown stack plume which also has an odor. Some SO_2 will often be formed in the concentrator by the reduction of sulfuric acid by organic compounds. No data of any value is available and SO_2 emission is not generally a problem. Both SO_2 emissions from this cause and acid mist will increase at high concentrations, and this type of equipment is not suitable for producing acid of a higher strength than 95-96%.

Plant Classifications 2.1, 2.2, 2.3, 2.4, 2.5

These classifications refer to future plants of the same types as discussed on the previous pages. They are considered separately only because the construction of a plant and control system simultaneously often produces different economic results.

Class 2.1, a 3-stage sulfur burning plant which is not presently being built may return to consideration if built in conjunction with a control system. It is quite possible that the trend to higher conversion of SO_2 to SO_3 in the converter may be reversed if a good method of recovering and recycling SO_2 from the stack is developed. Thus a plant incorporating a 3-stage converter operating with an SO_2 concentration of 10-12% and a conversion of 90-95% would represent a considerable capital cost saving over a modern 98% conversion plant. This capital cost saving would then contribute to the cost of the emission control plant designed to recover the unconverted SO_2 and return it to the plant inlet. At the present time a development of this kind represents the most likely approach to an overall 100% conversion SO_2 to acid.

Class 2.2 is a 4-stage sulfur burning plant of design similar to those presently being built. This is still the most popular plant but future plants may be of this type, arranged to include a tail gas recovery system, in which case they would be designed for maximum production regardless of conversion, and would recover SO_2 from tail gas for recycle. They might possibly be arranged to add processes 1.2.2 or 1.2.1 at a future time if emissions had not been specified. Of course, the use of a new dual absorption plant (1.1.0) is the other alternative.

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Classes 2.3 and 2.4 are new 3-stage and 4-stage "wet gas" plants, respectively. The comments on 2.1 and 2.2 above are equally applicable to these classifications, except that use of dual absorption would be greatly restricted as discussed in Parts IV and V.

Class 2.5 is a new concentrator, probably identical to those in existence in class 1.5.

Acid Production Cost

The cost of acid production for plants of classifications 1.0, 1.1, 1.2, 1.3 and 1.4 have been calculated as a basis for determination of "Control Cost" in Part V. The acid production cost is not intended to represent actual cost for any plant, but to provide a basis for control cost only, since unit costs used are the same before and after inclusion of a control system, and all processes are compared on the same basis. Changes in unit costs could conceivably alter the relative merits of the processes to some extent.

In determining operating costs the following conversion rates were assumed:-

Plant Classification 1.0	96.5%
Plant Classification 1.1	95
Plant Classification 1.2	96
Plant Classification 1.3	95.8
Plant Classification 1.4	96.8

The emission levels for class 1.1 and 1.2 were selected as typical for plants producing at maximum rate. The levels for 1.3 and 1.4 also fall within the ranges for these plants, however, these specific rates were selected to simplify calculations of control costs in Part V.

Unit costs selected for raw material and utilities are as follows:-

Sulfur	\$25 per short ton
Sulfur Value in Any Other Form (i. e. sludge, smelter gas, etc)	Zero
Electric Power	\$.01 per KWH
Cooling Water	\$.01 per short ton
Process Water	\$.02 per short ton
Boiler Feed Water	\$.05 per short ton
Steam	\$.60 per short ton

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Operating labor requirements for sulfur burning contact plants have been assumed to be one man per shift, plus part time supervision equivalent to 1/3 of a man per shift. This is not true for all plants, but is typical of the majority, since most acid plants are associated with other operations and may share some services. Operators have been charged at \$6 per hour and supervisors at \$8 per hour. Chamber plants, most of which are connected with small operations in the southeast where labor costs are generally lower and plants are older and less automated and may require more labor. In this case we have used the equivalent of 2-1/4 men per shift at \$4 per hour.

Maintenance for contact plants has been assumed to be approximately 4% of the capital investment per year, including materials and labor. For chamber plants, due to age and type of construction, 8% has been used. Overhead is assumed to be 100% of the labor component of maintenance plus operations, or approximately 70% of the sum of operations and maintenance.

Depreciation is on a 10 year, straight line basis, and interest is taken as 7-1/2% of investment per year. Since plants in classification 1.0, 1.1 and 1.3 are assumed to be pre-1960, and consequently over 10 years old, no operating cost is charged for depreciation and interest in these classifications.

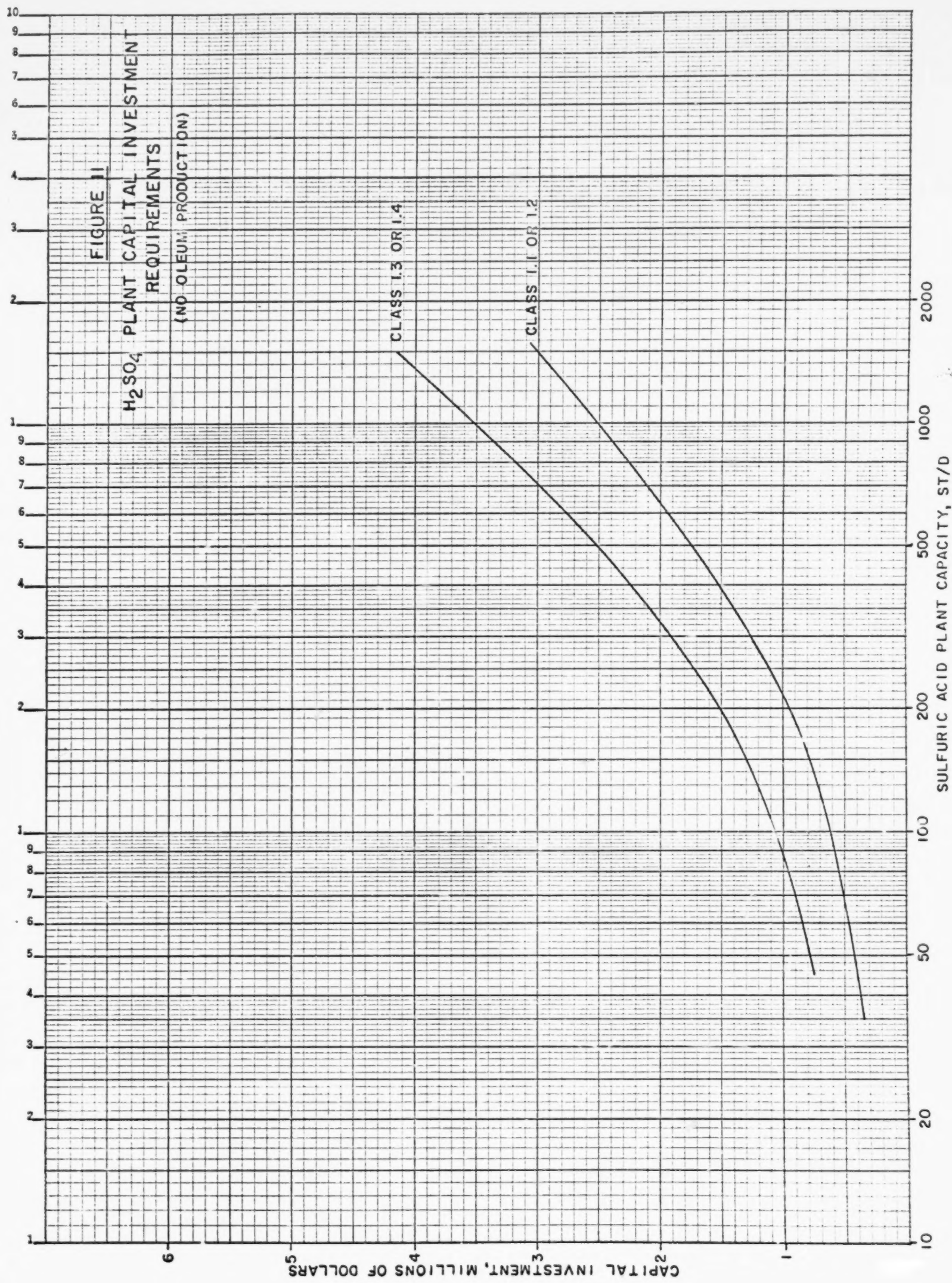
Taxes and insurance are assumed to be 1-1/2% of the original investment per year, except in the case of chamber plants where 1% has been used.

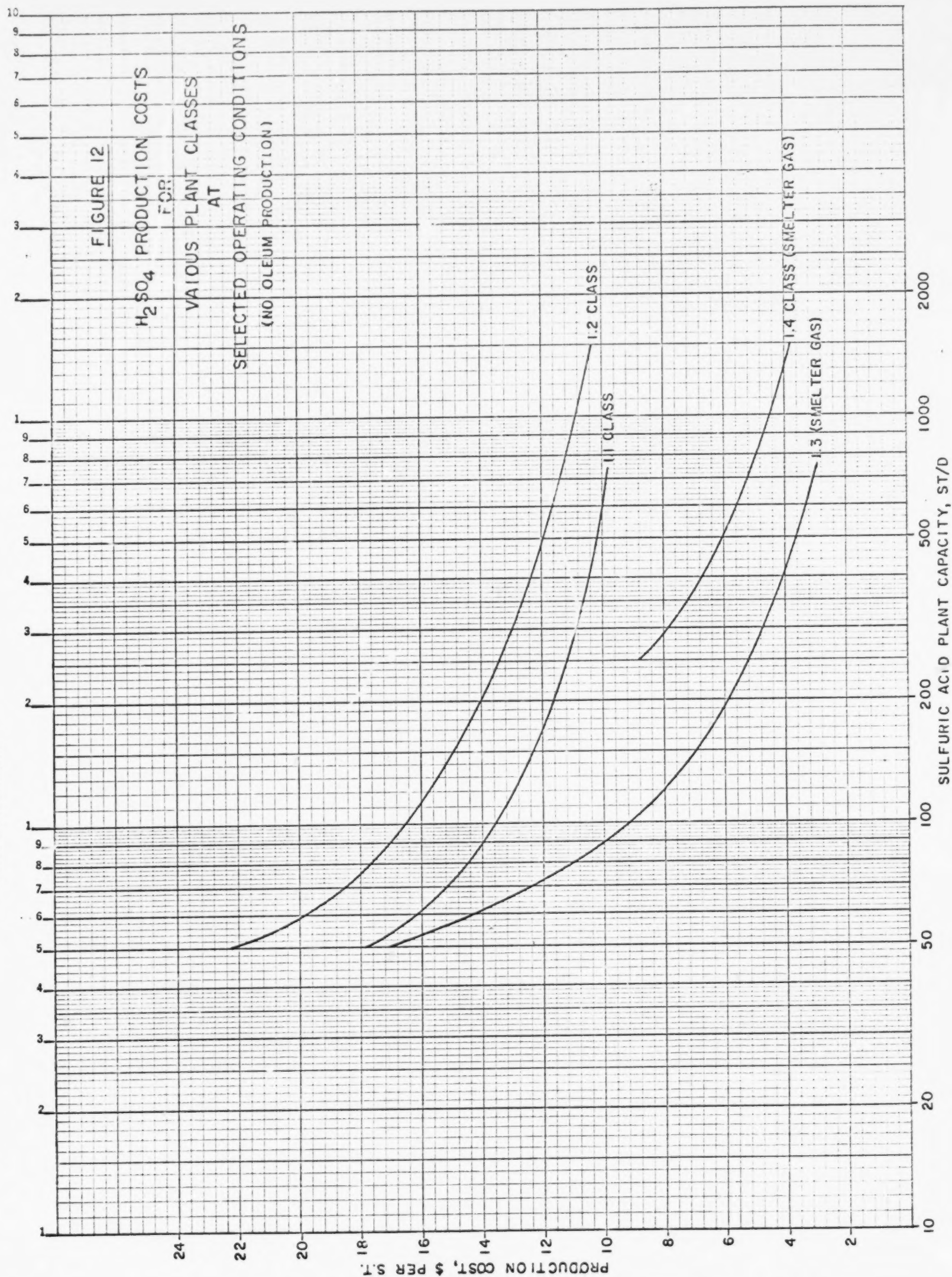
The capital costs upon which maintenance, depreciation, taxes and insurance are based are estimated typical single train battery limits plant costs in the United States. Battery limits, for this purpose, includes the erected cost, less land, of the equipment shown on Figures 5 through 10 illustrating the various plant classifications. For 1.3 and 1.4, a smelter gas plant has been used as typical.

Figure 11 shows approximate investment requirements upon which those portions of operating cost relating to initial investment are based. No investment difference is shown between 3 and 4-stage plants of the same type, since design improvements approximately offset increased costs for a number of years.

Figure 12 gives the acid production cost for various types of single unit plants from 50 to 1,500 T/D capacity based upon these parameters. Tables in the appendix show the basis of these curves. These costs are the basis for calculating control costs in Part V.

No production cost is given for concentrators, since a wide variety of capacities is possible with any one plant, capacity of a unit being determined by water removed, not the quantity of acid produced.





C. CENSUS OF SULFURIC ACID PLANTS

The census, which appears in Tables 4, 5 and 6, has been prepared as a tool to help determine the importance of various processes by determining the number of potential possible applications in the United States. The census is not represented as absolutely accurate or complete, since it is not based on a direct survey of acid manufacturers, but upon published data and in-house knowledge.

The census is divided into three parts; Table 4 lists chamber acid plants, Table 5 contact acid plants and Table 6 sulfuric acid drum type concentrators. Vacuum type concentrators have not been included, since they present no emission problem and require no consideration in this study.

The census is arranged geographically by states, listing each plant. Annual capacity is based upon approximately 330 operating days per year. Although the on-stream factor for most plants is higher than 330 days per year, all plants are not operating at full capacity at all times, thus 330 days equivalent is not an unrealistic figure.

The terms "unit", "plant" and "establishment" as used in this census require definition.

A unit may be considered as an individual H_2SO_4 production train, capable of independent operation to produce one or more grades of H_2SO_4 from one or more raw materials.

A plant is one or more units built at the same time and place. For example, Continental Oil at Pierce, Florida is a 2,000 T/D plant (Table 5) which consists of two - 1,000 T/D units in parallel, built simultaneously.

An establishment denotes one or more plants built and operated by one company at one location. An example is Valley Nitrogen at Helm, California, which includes 200, 300 and 600 ton plants built at different times, but at the same location for the same producer. For plants built after 1954, we have attempted to list each plant, but prior to 1954 have not attempted to differentiate between a plant and an establishment. For example, Cities Service Co. at Isabella, Tennessee (Table 5) is listed as a plant, but this is very likely more than one plant, judging by the capacity and date built. Where a range of years is given before 1954, the reason often is that an establishment consists of two or more plants built at various times within the given span of years.

For Table 5, the column headed "Principal Raw Materials" differentiates between sulfur burning plants (classifications 1.1 and 1.2) and wet gas plants (classifications 1.3 and 1.4). Sulfur burning plants list only sulfur as a raw material. Other plants, even though they may burn some sulfur, are wet gas plants, since their emission characteristics and selection of control methods will be determined by the non-sulfur raw material(s).

The column labeled "Highest Concentration Product" on Table 5 lists only 2 categories, since these determine the emission characteristics. An oleum plant may produce one or more oleum grades, and may also produce 98 or 93% acid, but as long as oleum is produced this fact

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governs the emission characteristics of the plant. Plants producing acid only below 99% H_2SO_4 have essentially the same emission problems, regardless of the grades produced.

Under the heading "Air Quality Control Region" is listed the central city of one of the first 57 Air Quality Control Regions selected by the National Air Pollution Control Administration (NAPCA).

If the geographic limits of the AQCRs have not yet been designated, we have assumed that the Standard Metropolitan Statistical Area (SMSA) will coincide with the AQCR. When a plant location falls within the AQCR (or equivalent SMSA), the fact is noted in this column. The first 57 AQCRs are listed on the following page.

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- | | | | |
|-----|-----------------------|-----|--------------------------------|
| 1. | Washington, D.C.* | 30. | Toledo |
| 2. | New York* | 31. | Steubenville-Wierton-Wheeling* |
| 3. | Chicago* | 32. | Chattanooga |
| 4. | Philadelphia* | 33. | Atlanta |
| 5. | Denver* | 34. | Memphis |
| 6. | Los Angeles* | 35. | Portland, Oregon |
| 7. | St. Louis* | 36. | Salt Lake City |
| 8. | Boston* | 37. | New Orleans |
| 9. | Cincinnati* | 38. | Miami |
| 10. | San Francisco* | 39. | Oklahoma City |
| 11. | Cleveland* | 40. | Omaha |
| 12. | Pittsburgh* | 41. | Honolulu |
| 13. | Buffalo* | 42. | Beaumont-Port Arthur |
| 14. | Kansas City* | 43. | Charlotte, N.C. |
| 15. | Detroit* | 44. | Portland, Maine |
| 16. | Baltimore* | 45. | Albuquerque |
| 17. | Hartford* | 46. | Lawrence-Lowell-Manchester |
| 18. | Indianapolis* | 47. | El Paso |
| 19. | Minneapolis-St. Paul* | 48. | Las Vegas |
| 20. | Milwaukee* | 49. | Fargo-Moorehead |
| 21. | Providence* | 50. | Boise |
| 22. | Seattle-Tacoma* | 51. | Billings |
| 23. | Louisville* | 52. | Sioux Falls |
| 24. | Dayton* | 53. | Cheyenne |
| 25. | Phoenix | 54. | Anchorage |
| 26. | Houston* | 55. | Burlington |
| 27. | Dallas-Ft. Worth* | 56. | San Juan |
| 28. | San Antonio* | 57. | Virgin Islands |
| 29. | Birmingham | | |

* Denotes those areas for which the AQCRs have been designated as of March 1, 1970.

SULFURIC ACID PLANT CENSUS

TABLE 4
CHAMBER PROCESS ACID PLANTS

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year (2) Built	Principal Raw Materials	Highest Concentration Product
Alabama	Standard Chemical	Troy	---	17,000	50	Pre 1954	Sulfur	< 78% Acid
	Horne Guano Co.	Dothan	---	13,500	40	"	"	"
	Mobil Chem. Co.	Mobile	---	17,000	50	"	"	"
Florida	Wilson Toomer Fert. Co.	Cottondale	---	15,000	45	1950	Sulfur	< 78% Acid
	Continental Oil Co./Agrico. Chem.	Pensacola	---	14,000	40	Pre 1954	"	"
	Wilson Toomer Fert. Co.	Jacksonville	---	40,000	120	1946	"	"
Georgia	Southern States Phosphate Fert.	Savannah	---	32,000	100	1917	Sulfur	< 78% Acid
	Mobil Chem. Co.	Savannah	---	20,000	60	1900	"	"
	Pelham Phos. Co.	Pelham	---	25,000	70	1912	"	"
	F. S. Royster Guano Co.	Athens	---	25,000	70	Pre 1954	"	"
	Armour Agr. Chemical Co.	Albany	---	20,000	60	"	"	"
	Armour Agr. Chemical Co.	Columbus	---	18,000	50	"	"	"
	Columbia Nitrogen Corp.	Moultrie	---	20,600	60	"	"	"
	Continental Oil Co./Agrico Chem.	Savannah	---	20,000	60	"	"	"
	Cotton States Fertilizer Co.	Macon	---	16,000	45	"	"	"
	Georgia Fert. Co.	Valdosta	---	20,000	60	"	"	"
	Mobil Chem. Co.	Rome	---	18,000	50	"	"	"
Illinois	Armour Agr. Chemical Co.	Chicago Hqts.	Chicago	35,000	100	Pre 1954	Sulfur	< 78% Acid
	Continental Oil Co./Agrico Chem.	Fulton	---	16,000	45	"	"	"
	Continental Oil Co./Agrico Chem.	Humboldt	---	25,000	70	Pre 1954	Sulfur	< 78% Acid
Iowa	Kerr McGee Chem. Corp.	Baltimore	Baltimore	105,000	300	1917	Sulfur	< 78% Acid
	F. S. Royster Guano Co.	Baltimore	Baltimore	40,000	120	Pre 1954	"	< 76% Acid
	Continental Oil Co./Agrico Chem.	Baltimore	Baltimore	34,000	100	"	"	"
Mississippi	Inter Min. & Chem. Corp.	Tupelo	---	18,000	50	Pre 1954	Sulfur	< 78% Acid
	Continental Oil Co./Agrico Chem.	Greensboro	---	21,000	60	Pre 1954	Sulfur	< 78% Acid
	Mobil Chem. Co.	Charleston	---	18,000	50	1900	Sulfur	< 78% Acid
N. Carolina	Planters Fert. Phosphate Co.	Charleston	---	25,000	70	Pre 1954	"	"
	F. S. Royster Guano Co.	Charleston	---	12,000	35	"	"	"
	Anderson Fertilizer Co.	Anderson	---	17,000	50	"	"	"
S. Carolina	Continental Oil Co./Agrico Chem.	Charleston	---	20,000	60	"	"	"
	Continental Oil Co./Agrico Chem.	Columbia	---	11,000	35	"	"	"
	Inter Min. & Chem. Corp.	Spartanburg	---	20,000	60	"	"	"
Tennessee	Mobil Chem. Co.	Memphis	Memphis (1)	18,000	50	1903	Sulfur	< 78% Acid
Virginia	Mobil Chem. Co.	Richmond	---	35,000	100	1912	Sulfur	< 78% Acid
	F. S. Royster Guano Co.	Norfolk	---	22,000	65	Pre 1954	"	"
	American Agr.	Alexandria	National Capital	20,000	60	"	"	"
	W. R. Grace & Co.	Norfolk	---	22,000	65	"	"	"

Total - 37 Plants Producing 885,100 Short Tons/Yr.
Total Within AQCR - 6 Plants Producing 262,000 Short Tons/Yr.

NOTES:

- (1) AQCR not yet designated; plant located within SMSA.
- (2) Where pre 1954 is given, exact date was not available.

SULFURIC ACID PLANT CENSUS

TABLE 5

CONTACT PROCESS ACID PLANTS

State	Company	City	Air Quality Control Region (1)	Annual Capacity Short Tons	Daily Capacity Short Tons	Year Built (2)(3)	Principal Raw Materials	Highest Concentration Product
Alabama	Mobil Chem. Co.	Birmingham	Birmingham	26,000	70	1938	Sulfur	<99% Acid
	American Cyanamid Co.	Mobile	---	28,000	75	1947	"	"
	Mobil Chem. Co.	Dothan	---	26,000	70	1966	"	"
	DuPont	Mineral Springs	---	21,000	60	Pre 1954	"	Oleum
	Reichhold Chem. Inc.	Tuscaloosa	---	52,000	150	1956	"	"
	Stauffer Chem. Co.	LeMoyne	---	140,000	400	1956	"	"
Arizona	Arizona Agrochemical Corp.	Chandler	Phoenix (1)	28,000	85	1959	Sulfur	<99% Acid
	Bagdad Copper Corp.	Bagdad	---	60,000	175	1961	"	"
	Phelps Dodge Corp.	Morenci	---	210,000	600	1965	Cu Smelter Gas	Oleum
	Phelps Dodge Corp.	Morenci	---	59,500	175	1968	"	"
	Kennecott Copper Corp.	Ray	---	262,000	750	1968	"	<99% Acid
	Monsanto Co.	ElDorado	---	132,000	375	Pre 1954	Sulfur	<99% Acid
Arkansas	Arkla Chemical Corp.	Helena	---	210,000	600	1967	Sulfur & Hydrogen Sulfide	Oleum
	Olin	N. Little Rock	---	87,000	250	1947	"	"
California	Allied Chemical Corp.	Nichols	San Francisco Bay	120,000	350	Pre 1954	Sulfur	<99% Acid
	Occidental Petroleum Corp.	Lathrop	---	245,000	700	1957	"	"
	Valley Nitrogen Prod. Inc.	Helm	---	70,000	200	1959	"	"
	Valley Nitrogen Prod. Inc.	Helm	---	105,000	300	1963	"	"
	Valley Nitrogen Prod. Inc.	Helm	---	210,000	600	1965	"	"
	AFC Inc.	Edison	---	67,500	200	1967	"	"
	Monsanto Co.	Avon	San Francisco Bay	105,000	300	1953	Sludge & Hydrogen Sulfide	Oleum
	American Smelting & Refining	Selby	San Francisco Bay	15,000	50	Pre 1954	Smelter Gas	<99% Acid
	Allied Chemical Corp.	El Segundo	Los Angeles	140,000	400	Pre 1954	Sludge & Hydrogen Sulfide	"
	Stauffer Chem. Co.	Dominguez	Los Angeles	230,000	650	Pre 1954	"	"
	Allied Chemical Corp.	Richmond	San Francisco Bay	65,000	200	1943	"	"
	Allied Chemical Corp.	Richmond	San Francisco Bay	113,000	300	1955	"	"
	Union Oil Co. of California	Los Angeles	Los Angeles	175,000	500	Pre 1954	Sulfur	Oleum
	Stauffer Chem. Co.	Richmond	San Francisco Bay	105,000	300	Pre 1954	"	"
	Stauffer Chem. Co.	Vernon	Los Angeles	297,500	850	1969	"	"
	Stauffer Chem. Co.	Martinez	San Francisco Bay	60,000	175	1960-65	Sulfur	<99% Acid
Colorado	Union Carbide Corp.	Uravan	---	50,000	150	Pre 1954	Pyrites	Oleum
Delaware	Allied Chemical Corp.	Denver	Denver	350,000	1,000	Pre 1954	Sludge + Pyrites	Oleum
	Allied Chemical Corp.	N. Claymont	Philadelphia			Pre 1954		

TABLE 5 - PAGE 2

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year (2)(3) Built	Principal Raw Materials	Highest Concentration Product
Florida	Mobil Chem. Co.	Nichols	---	110,000	300	Pre 1954	Sulfur	<99% Acid
	American Cyanamid Co.	Brewster	---	320,000	900	Pre 1954	"	"
	W. R. Grace & Co.	Bartow	---	230,000	700	Pre 1954	"	"
	Inter. Min. & Chem. Corp.	Bartow	---	210,000	600	Pre 1954	"	"
	Swift & Co.	Agricola	---	315,000	900	1948	"	"
	Mobil Chem. Co.	Nichols	---	200,000	600	1955-59	"	"
	American Cyanamid Co.	Brewster	---	260,000	750	1955	"	"
	Cities Service Co. Inc.	Tampa	---	300,000	900	1955-59	"	"
	Cities Service Co. Inc.	Tampa	---	300,000	900	1955-59	"	"
	Cities Service Co. Inc.	Tampa	---	300,000	900	1955-59	"	"
	W. R. Grace & Co.	Bartow	---	230,000	700	1955-59	"	"
	F. S. Royster Guano Co.	Mulberry	---	385,000	1,100	1960-65	"	"
	Mobil Chem. Co.	Nichols	---	225,000	650	1960-65	"	"
	American Cyanamid Co.	Brewster	---	50,000	150	1960	"	"
	Chemical Inc.	Bartow	---	315,000	900	1960-65	"	"
	Inter. Min. & Chem. Corp.	Bartow	---	210,000	600	1960-65	"	"
	Chemical Inc.	Bartow	---	140,000	400	1960-65	"	"
	Armour Agr. Chemical Co.	Bartow	---	315,000	900	1962	"	"
	Armour Agr. Chemical Co.	Ft. Meade	---	520,000	1,500	1963	"	"
	Chemical Inc.	Bartow	---	280,000	800	1964	"	"
	Continental Oil Co. / Agrico Chem.	Bartow	---	315,000	900	1964	"	"
	Borden Chem. Co. / Smith Douglas	Pierce	---	700,000	2,000	1964	"	"
	Central Phosphates Inc.	Plant City	---	490,000	1,400	1966	"	"
	Farmland Ind. Inc.	Green Bay	---	600,000	1,700	1966	"	"
	W. R. Grace & Co.	Bartow	---	550,000	1,570	1966	"	"
	Occidental Petroleum Corp.	White Springs	---	365,000	1,100	1966	"	"
	Kaiser Agr. Chem. Company	White Springs	---	700,000	2,000	1966	"	"
	American Cyanamid Co.	Savannah N.	---	35,000	100	1952	Sulfur	<99% Acid
	American Cyanamid Co.	Savannah	---	160,000	450	1953	"	"
	Minerals & Chem. / Philipp Corp.	Savannah	---	85,000	250	1956	"	"
	Cities Service Co. Inc.	Attapulgas	---	36,000	100	1956	"	"
	Standard Oil Co. of California	Augusta	---	131,200	375	1967	"	"
Hawaii		Honolulu	(1)	40,000	115	1950-65	Sludge	<99% Acid
	J. R. Simplot Co.	Pocatello	---	225,000	650	1959	Sulfur	<99% Acid
Idaho	J. R. Simplot Co.	Pocatello	---	420,000	1,200	1966	"	"
	Bunker Hill Co.	Kellogg	---	90,000	250	1954	Zn Smelter Gas	"
	Bunker Hill Co.	Kellogg	---	120,000	350	1966	"	"

TABLE 5 - PAGE 3

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year Built (2)(3)	Principal Raw Material	Highest Concentration Product
Illinois	Allied Chemical Corp.	Chicago	Chicago	130,000	400	Pre 1954	Sulfur	<99% Acid
	Swift & Co.	Calumet City	Chicago	35,000	100	1947	"	"
	Borden Chem. Co./Smith Douglas	Streator	---	43,000	125	1951	"	"
	National Distillers Chem. Corp.	Tuscola	---	175,000	500	1953	"	"
	American Zinc Co.	Sauget	---	140,000	400	1960-65	"	"
	Hooker Chem. Corp.	Marseilles	---	240,000	700	1962	"	"
	Wilson Co. Inc.	Elwood	Chicago	210,000	600	Pre 1954	Sulfur + Sludge	Oleum
	Charles Pfizer Co. Inc.	East St. Louis	St. Louis	6,000	18	Pre 1954	Ferrous Sulfate	<99% Acid
	American Zinc Co.	East St. Louis	St. Louis	154,000	450	1967	Zn Smelter Gas	"
	Monsanto Co.	Monsanto	St. Louis	234,000	675	Pre 1954	Sulfur	Oleum
	New Jersey Zinc Co.	Depue	---	420,000	1,200	1967	Zn Smelter Gas + Sulfur	<99% Acid
	Allied Chemical Corp.	East St. Louis	St. Louis	180,000	500	1928	Sulfur	Oleum
	Olin	Joliet	Chicago	350,000	1,000	1942	"	"
	American Cyanamid Co.	Joliet	Chicago	50,000	150	1954	"	"
	Monsanto Co.	Monsanto	St. Louis	140,000	400	1955	"	"
Indiana	Stauffer Chem. Co.	Hammond	Chicago	140,000	400	1929	Sludge + Sulfur	Oleum
	DuPont	East Chicago	Chicago	325,000	950	Pre 1954	Zn Smelter Gas + Sludge	"
	Stauffer Chem. Co.	Hammond	Chicago	165,000	500	1957	Sludge + Sulfur	"
	Marion Mfg. Co.	Indianapolis	Indianapolis	42,000	125	1947	Sludge + Sulfur	"
Iowa	Inter. Min. + Chem. Corp.	Mason City	---	25,000	70	Pre 1954	Sulfur	<99% Acid
	Sinclair Petrochemicals Inc.	Ft. Madison	---	525,000	1,500	1968	"	"
	National Distillers Chem. Corp.	Dubuque	---	52,000	150	1943	"	Oleum
Kansas	Eagle Picher Co.	Galena	---	155,000	450	1954	Sulfur + Zn Smelter Gas	<99% Acid
	National Distillers Chem. Corp.	DeSoto	Kansas City	88,000	250	1943	Sulfur	Oleum
Kentucky	DuPont	Wurtland	---	210,000	600	Pre 1954	Sulfur	Oleum
	Pennsalt Chem. Corp.	Calvert City	---	44,000	125	1948	"	"
Louisiana	Olin	Bossier City	---	70,000	200	1929	Sulfur	<99% Acid
	Allied Chemical Corp.	Baton Rouge	---	87,000	250	1954	"	"
	American Cyanamid Co.	Fortier	New Orleans	35,000	100	1960-65	"	"
	Hooker Chem. Corp.	Taft	---	510,000	1,500	1965	"	"
	Allied Chemical Corp.	Geismar	---	525,000	1,500	1967	"	"
	Freeport Sulphur Co.	Convent	---	1,680,000	4,800	1968	"	"
	Stauffer Chem. Co.	Baton Rouge	---	560,000	1,600	1969	Sulfur + Sludge	Oleum
	Cities Service Co. Inc.	Lake Charles	---	149,000	450	1943	Sludge + Hydrogen Sulfide	<99% Acid
	DuPont	Burnside	---	525,000	1,500	1967	Sulfur + Sludge	Oleum
	Bethlehem Steel Corp.	Sparrows Pt.	Baltimore	87,000	250	1953	Pyrites + Hydrogen Sulfide	<99% Acid
	Olin	Baltimore	Baltimore	105,000	300	1943	Sulfur	Oleum
	Olin	Baltimore	Baltimore	70,000	200	1941	"	"
	Olin	Baltimore	Baltimore	175,000	500	1949	"	"
	W. R. Grace & Co.	Baltimore	Baltimore	140,000	400	1960-65	"	"
Maryland	Bethlehem Steel Corp.	Sparrows Pt.	Baltimore	87,000	250	1953	Pyrites + Hydrogen Sulfide	<99% Acid
	Olin	Baltimore	Baltimore	105,000	300	1943	Sulfur	Oleum

TABLE 5 - PAGE 4

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year Built (2)(3)	Principal Raw Material	Highest Concentration Product
Massachusetts	Monsanto Co.	Everett	Boston	105,000	300	1969	Sulfur	Oleum
Michigan	W. R. Grace & Co. American Cyanamid Co. Continental Oil Co./Agrico Chem. Allied Chemical Corp.	Detroit Kalamazoo Bay City Detroit	Detroit	35,000 25,000 35,000 10,000	100 70 100 600	Pre 1954 1947 1957 1941	Sulfur " " Sulfur + Sludge	<99% Acid " Oleum
Minnesota	North Star Chem. Inc.	Pine Bend	Minneapolis-St. Paul	115,000	330	1959	Sulfur	<99% Acid ^d
Mississippi	Coastal Chem. Corp.	Pascagoula	---	260,000	750	1958	Sulfur	<99% Acid
Missouri	Missouri Lead Smelting Co. St. Joseph Lead W. R. Grace & Co. National Lead Co. National Lead Co. National Lead Co.	Salem Herculaneum Joplin St. Louis St. Louis St. Louis	St. Louis --- --- St. Louis St. Louis St. Louis	70,000 110,000 70,000 70,000 160,000 160,000	200 350 200 200 450 450	1967 1969 1960-65 1945 1950 1957	Zn or Pb Smelter Gas Pb Smelter Gas Sulfur " " " " " "	<99% Acid " Oleum <99% Acid " "
Montana	Anaconda Co.	Anaconda	---	155,000	450	Pre 1954	Zn Smelter Gas	<99% Acid
Nevada	Anaconda	Yerington	---	130,000	400	1953	Sulfur + Ore	<99% Acid
New Jersey	La Place Chem. Co. National Lead Co. National Lead Co. National Lead Co. National Lead Co. Olin Allied Chemical Corp. Allied Chemical Corp. DuPont DuPont DuPont American Cyanamid Co. American Cyanamid Co. Essex Chem Corp./Chems. Div.	Edison Sayreville Sayreville Sayreville Sayreville Paulsboro Elizabeth Gibbstown Linden Deepwater Warners Bound Brook Newark	N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. Philadelphia N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. Philadelphia N.Y.-N.J.-Conn. Philadelphia N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. N.Y.-N.J.-Conn. N.Y.-N.J.-Conn.	70,000 105,000 105,000 160,000 160,000 300,000 200,000 220,000 100,000 300,000 120,000 197,000 64,000 180,000	200 300 300 450 450 850 600 600 300 850 350 550 200 500	Pre 1954 1947 1948 1950 1955 1959 1957 1957 Pre 1954 Pre 1954 Pre 1954 1928 1940 1956	Sulfur " " " " " " " " Sulfur + Sludge " " " " Sulfur " " " " " " " " " "	<99% Acid " Oleum " " " <99% Acid " Oleum " " " " "
New Mexico	Kerr McGee Chem. Corp. Climax Chemical Co.	Grants Hobbs	---	140,000 53,000	400 150	1958 1962	Sulfur Sulfur + Hydrogen Sulfide	<99% Acid "
New York	Allied Chemical Corp. Eastman Kodak Co.	Buffalo Rochester	Niagara Frontier	195,000 7,000	550 20	Pre 1954 1930	Sulfur " "	Oleum "
N. Carolina	Mobil Chem. Co. Swift Co. Acme Chemical Texas Gulf Sulphur Co. Armour Agr. Chemical Co.	Wilmington Wilmington Acme Lee Creek Wilmington	---	25,000 50,000 55,000 1,087,500 70,000	70 150 170 3,050 200	1944 1955 1964 1966 1968	Sulfur " " " " " " " "	<99% Acid " " " "

TABLE 5 - PAGE 5

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year Built (2)(3)	Principal Raw Material	Highest Concentration Product
Ohio	Allied Chemical Corp.	Cleveland	Cleveland	125,000	350	Pre 1954	Sulfur	<99% Acid
	Diamond Fertilizer Co.	Sandusky	---	11,000	35	Pre 1954	"	"
	DuPont	Cleveland	Cleveland	200,000	600	Pre 1954	"	"
	Inter. Min. & Chem. Corp.	Leckland	Cincinnati	35,000	100	Pre 1954	"	"
	Mobil Chem. Co.	Cincinnati	Cincinnati	14,000	40	1938	"	"
	Munn. Muning & Mfg. Co.	Copley	Cincinnati	60,000	175	1942	"	"
	American Cyanamid Co.	Hamilton	Cincinnati	90,000	250	1955	"	"
	Continental Oil Co. / Agrico Chem.	Cairo	---	43,500	125	1960	"	"
	American Zinc Co.	Columbus	---	70,000	200	1967	Zn Smelter Gas	"
	DuPont	North Bend	Cincinnati	105,000	300	1955-59	Sulfur	Oleum
Oklahoma	Ozark Mahoning Co.	Tulsa	---	120,000	360	1941	Hydrogen Sulfide	<99% Acid
Pennsylvania	National Zinc	Bartlesville	---	65,000	200	Pre 1954	Zn Smelter Gas + Sulfur	"
	New Jersey Zinc Co.	Palmerton	---	180,000	500	Pre 1954	Zn Smelter Gas	Oleum
	Witco Chem. Co. Inc.	Petrolia	Pittsburgh	35,000	100	1933	Sludge + Sulfur	"
	Atlantic Richfield Co.	Philadelphia	Philadelphia	140,000	400	1953-59	Sludge + Hydrogen Sulfide	"
	DuPont	Cornwells Hts.	Philadelphia	70,000	200	Pre 1954	Unknown	<99% Acid
	Allied Chemical Corp.	Newell	Pittsburgh	250,000	700	Pre 1954	Sulfur + Pyrite + Sludge	"
	U. S. Steel Corp.	Neville Island	Pittsburgh	45,000	125	Pre 1954	Sulfur + Hydrogen Sulfide	"
	Charles Pfizer Co. Inc.	Easton	---	12,200	35	1967	Ferrous Sulfate	"
	St. Joseph Lead	Josephstown	Pittsburgh	100,000	300	1968	Zn Smelter Gas	"
	Rohm and Haas Co.	Philadelphia	Philadelphia	88,000	250	1929-54	Sulfur	"
Rhode Island	Essex Chemical	E. Providence	Providence	17,000	50	1929-49	Sulfur	<99% Acid
S. Carolina	W. R. Grace & Co.	Charleston	---	35,000	100	1955-59	Sulfur	<99% Acid
	Cities Service Co. Inc.	Copperhill	---	280,000	800	Pre 1954	Pyrites	Oleum
Tennessee	Cities Service Co. Inc.	Isabella	---	700,000	2,000	Pre 1954	Pyrites	<99% Acid
	Volunteer Ordnance	Tyner	Chattanooga	145,000	400	Pre 1954	Sulfur	Oleum
Texas	Olin	Pasadena	Houston	210,000	600	1947	Sulfur	<99% Acid
	Borden Chem. Co. / Smith Douglas	Texas City	---	155,000	450	1953	"	"
	Phosphate Chem. Inc.	Pasadena	Houston	420,000	1,200	1960-65	"	"
	Potash Co. of America	Machovec	---	15,000	45	1960-65	"	"
	Occidental Petroleum Corp.	Plainview	---	105,000	300	1963	"	"
	American Plant Food Corp.	Galena Park	Houston	140,000	400	1965	"	"
	American Smelting & Refining Co.	Corpus Christi	---	70,000	200	Pre 1954	Zn Smelter Gas	Oleum
	DuPont	La Porte	Houston	85,000	250	1955-59	Sludge + Sulfur	"
	DuPont	La Porte	Houston	285,000	750	1961	"	"
	Gulf Oil Corp.	Port Arthur	Beaumont-Pt. Arthur	105,000	300	Pre 1954	Sludge + Hydrogen Sulfide	<99% Acid
	Stauffer Chem. Co.	Baytown	Houston	275,000	800	1955	Sludge	"
	Olin	Beaumont	Beaumont-Pt. Arthur	180,000	500	1957	Sludge + Hydrogen Sulfide	<99% Acid
	Shamrock Oil & Gas Corp.	Dumas	---	32,000	100	1958	"	"
	Texaco Inc.	Port Arthur	Beaumont-Pt. Arthur	92,400	250	1965	"	"
	American Oil	Texas City	---	173,200	500	1969	Sludge	"
	Olin	Port Arthur	Beaumont-Pt. Arthur	70,000	200	Pre 1954	"	Oleum
	Stauffer Chem. Co.	Houston	Houston	629,000	1,750	Pre 1954	"	"
	Stauffer Chem. Co.	Ft. Worth	Dallas-Ft. Worth	120,000	350	Pre 1954	"	"
	Stauffer Chem. Co.	Houston	Houston	700,000	2,000	1967	"	"

TABLE 5 - PAGE 6

State	Company	City	Air Quality Control Region	Annual Capacity Short Tons	Daily Capacity Short Tons	Year Built (2)(3)	Principal Raw Material	Highest Concentration Product
Utah	AZ Minerals Corp.	Mexican Hat	---	28,000	100	1957	Sulfur	<99% Acid
	Kennecott Copper Corp.	Magna	Salt Lake City (1)	260,000	750	Pre 1954	Cu Smelter Gas	"
	Kennecott Copper Corp.	Magna	Salt Lake City (1)	140,000	400	1955-59	"	"
	Kennecott Copper Corp.	Magna	Salt Lake City	175,000	500	1967	"	"
Virginia	American Cyanamid Co.	Piney River	---	30,000	85	1930	Sulfur	<99% Acid
	Borden Chem. Co./Smith Douglas	Norfolk	---	70,000	200	1937	"	"
	Allied Chemical Corp.	Front Royal	---	140,000	400	1945	"	"
	Swift & Co.	Buell	---	47,000	135	1947	"	"
	Weaver Fertilizer Co. Inc.	Norfolk	---	30,000	100	1955-59	"	"
	Allied Chemical Corp.	Hopewell	---	140,000	400	1966	"	"
	DuPont	Richmond	---	90,000	250	Pre 1954	"	"
	Hercules Powder	Radford	---	25,000	70	Pre 1954	"	Oleum
Washington	Georgia-Pacific Corp.	Bellevue	---	10,000	30	1965	Sulfur	<99% Acid
	American Smelting & Refining Co.	Tacoma	Seattle-Tacoma	70,000	200	Pre 1954	Smelter Gas	"
	Allied Chemical Corp.	Anacortes	---	40,000	125	1958	Sludge + Hydrogen Sulfide + Sulfur	"
W. Virginia	Allied Chemical Corp.	Nitro	---	135,000	400	1948	Sulfur	<99% Acid
Wisconsin	DuPont	Barksdale	---	35,000	100	Pre 1954	Sulfur	Oleum
	Olin	Baraboo	---	70,000	200	Pre 1954	"	"
Wyoming	Western Nuclear Inc.	Riverton	---	70,000	200	1958	Sulfur	<99% Acid
	Western Nuclear Inc.	Jeffrey City	---	44,000	125	1962	"	"
	Totals - 214 Plants in 179 Establishments Producing -			37,722,500 Short Tons/Yr.				
	Within AQCRs Totals - 93 Plants in 79 Establishments Producing -			13,721,400 Short Tons/Yr.				

NOTES:

- (1) AQCR not yet designated; plant located within SMSA.
- (2) Where pre 1954 is given, exact date was not available.
- (3) Where two dates are given, year built is within the span given, but exact date was not available.

SULFURIC ACID PLANT CENSUS

TABLE 6

DRUM TYPE SULFURIC ACID CONCENTRATORS

<u>State</u>	<u>Company</u>	<u>City</u>	<u>Air Quality Control Region</u>	<u>No. of Units</u>	<u>Year Built</u>
Alabama	Alabama Ord. Works	Sylacauga	---	9	1942
Arkansas	Maumelle Ord. Works	Marche	---	8	1941
	Monsanto	El Dorado	---	1	1960
Illinois	Kankakee Ord. Works	Elwood	Chicago	7	1942
	Standard Oil Co. of Ind.	Wood River	St. Louis	1	1943
Indiana	Wabash River Ord. Works	Dana	---	9	1942
Kansas	Sunflower Ord. Works	Eudora	---	8	1942
Kentucky	Kentucky Ord. Works	Paducah	---	6	1942
Louisiana	Rubicon Chemicals	Geismar	---	1	1964
Minnesota	Gopher Ord. Works	Rosemount	Minneapolis-St. Paul	5	1942
Missouri	Weldon Spring Ord. Works	Weldon Spring	St. Louis	16	1941
New Jersey	American Cyanamid	Bound Brook	N. Y. - N. J. - Conn.	1	1941
	DuPont	Gibbstown	Philadelphia	1	1963
	DuPont	Gibbstown	Philadelphia	1	1966
Ohio	Plum Brook Ord. Works	Sandusky	---	12	1941
Oklahoma	Oklahoma Ord. Works	Pryor	---	9	1941
Pennsylvania	Pennsylvania Ord. Works	Williamsport	---	12	1942
	Keystone Ord. Works	Geneva	---	10	1942
	Allied Chemical	Newell	Pittsburgh	1	1962
Tennessee	Chickasaw Ord. Works	Memphis	Memphis (1)	2	1942
	Holston Ord. Works	Kingsport	---	7	1942
	Volunteer Ord. Works	Tyner	Chattanooga (1)	9	1942
Texas	Texaco	Port Arthur	Beaumont-Port Arthur (1)	2	1942
	Longhorn Ord. Works	Karnack	---	6	1942
Utah	Utah Oil Refining Co.	Salt Lake City	Salt Lake City (1)	1	1943
W. Virginia	W. Virginia Ord. Works	Pt. Pleasant	---	12	1942
	American Cyanamid	Willow Island	---	1	1957
	Allied Chemical	Moundsville	---	1	1964
	Carbide & Carbon Chem. Co.	Institute	---	1	1966

Total - 28 Establishments With 29 Plants and 160 Units

Within AQCRs Total - 11 Establishments With 12 Plants and 47 Units

NOTES:

(1) AQCR not yet designated; plant located within SMSA.

IV

EMISSION CONTROL SYSTEMS

A. SURVEY OF AVAILABLE SYSTEMS

Many systems for emission control for sulfuric acid plants and other stationary sources have appeared in the literature, a few of which are in commercial operation. Some have been extensively tested in the laboratory, and in a pilot scale unit, but the majority have been tested only in part, are patents untested on a continuous basis or actual conditions, or represent undeveloped ideas.

Since SO_2 and mist control in all cases represents an addition to the cost of producing acid, there has been no commercial incentive to develop control processes or devices beyond the economic use of raw materials and the requirements of a social nature imposed by local governmental authorities. The majority of commercially operating control systems have been in the area of mechanical devices for acid mist control, since the presence of acid mist is the easiest to detect and produces direct effects which tend to evoke immediate complaints from owners of adjacent properties. Mist control is also relatively inexpensive.

Control systems may be classified both by capabilities and by type of system, but since many systems which are basically the same can be operated in such a manner that different results may be achieved we have classified the various systems by types.

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Processes have been divided into four groups, the first three of which are most significant:-

- 1. x. x In plant modifications for SO₂ control.
- 2. x. x Tail gas treatment systems for SO₂, SO₃ and mist control.
- 3. x. x Mechanical devices and systems control of mist in tail gas.
- 4. x. x Systems applicable to chamber process acid plants.

These classifications have been further subdivided, as follows, using the second digit to denote the following:-

- 1. 1. x Systems applicable to new plants only.
- 1. 2. x Systems applicable to new or existing plants.
- 1. 3. x Methods of conversion improvement.
- 2. 1. x Systems recovering sulfur values as salable by-product.
- 2. 2. x Systems recovering sulfur values as additional acid product.
- 2. 3. x Systems recovering sulfur values as disposable solid waste product.
- 2. 4. x Systems recovering sulfur values partly as additional acid product and partly as salable by-products.
- 3. 1. x Mechanical devices.
- 3. 2. x Electro-mechanical devices.
- 3. 3. x Liquid absorbent systems.
- 3. 4. x Solid absorbent systems.

The third number, which identifies a process within a category, was assigned arbitrarily as the processes were added to the survey, and has no particular significance beyond identification.

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In general, processes in group 1 control SO_2 emission, those in group 2 control SO_2 , SO_3 and acid mist emission, those in group 3 are for acid mist control only, and those in group 4 are for SO_2 and NO_x control. Some group 2 processes may be used for SO_2 control only at reduced operating cost. This will be discussed further in Part V.

The processes surveyed are listed below by identification number and name. A process survey sheet on each of these processes appears in the appendix.

<u>Number</u>	<u>Name</u>
1.1.1	Dual Absorption (New Plant)
1.2.1	Add-On Dual Absorption using Converter Heat
1.2.2	Add-On Dual Absorption using Furnace Heat
1.2.3	Add-On Dual Absorption using Outside Heat Source
1.3.1	Ultraviolet Oxidation of SO_2
1.3.2	Ozone Injection to Catalyze Oxidation of Remaining SO_2
1.3.3	Formation of Oxysulfuric Acid to Oxidize Remaining SO_2
1.3.4	SO_2 - SO_3 Conversion Improvement by Plant Adjustments
2.1.1	Na_2CO_3 Absorption of SO_2 to Produce Na_2SO_3
2.1.2	MgO Absorption of SO_2 to Produce MgSO_4
2.1.3	Lime Absorption of SO_2 to Produce Plaster of Paris
2.1.4	Absorption with Ammonia-Oxidation of $(\text{NH}_4)_2\text{SO}_3$ to $(\text{NH}_4)_2\text{SO}_4$
2.1.5	SO_2 to Convert Phosphate Rock to Saleable Fertilizer
2.1.6	The Production of Peroxydisulfuric Acid to Absorb and Oxidize SO_2
2.1.7	Oxidation of SO_2 in Air- SO_2 Battery
2.1.8	Oxidation of SO_2 in Selenium Oxide Slurry

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<u>Number</u>	<u>Name</u>
2.1.9	SO ₂ Absorption with Na ₂ CO ₃ to Produce Na ₂ SO ₄
2.2.1	Absorption and Recovery of SO ₂ with Na ₂ SO ₃ -NaHSO ₃ Solution
2.2.2	SO ₂ Absorption with Na ₂ SO ₃ -NaHSO ₃ Solution; Recovery of SO ₂ with ZnO. Sodium Sulfite-Bisulfite and Zinc Oxide.
2.2.3	Absorption of SO ₂ with MnO ₂ -Mg(OH) ₂ and Recovery by Calcination (Grillo Process)
2.2.4	Absorption of SO ₂ with NaOH Solution; Recovery of SO ₂ and NaOH with Reducing Agent
2.2.5	Absorption of SO ₂ with Na ₂ CO ₃ and Reduction to Sulfur with CO+H ₂ Reform Gas
2.2.6	Magnesium Oxide Absorption of SO ₂ with SO ₂ Recovery
2.2.7	Absorption and Recovery of SO ₂ with MgSO ₃ -Mg(HSO ₃) ₂ Solution
2.2.8	Potassium Sulfite-Bisulfite
2.2.9	SO ₂ Absorption with K ₃ PO ₄ to Form K ₂ S ₂ O ₅ and its Conversion to Sulfur
2.2.10	Absorption of SO ₂ by K ₂ SO ₃ -KHSO ₃ ; Recovery of SO ₂ with Aldehyde Bisulfite
2.2.11	Absorption with Ammonia-Recovery of SO ₂ from Ammonia Bisulfite
2.2.12	Absorption of SO ₂ with Ammonium Sulfite and Bisulfite; Recovery of SO ₂ with ZnO
2.2.13	Absorption of SO ₂ with Manganese Oxides with Recovery of SO ₂ From MnSO ₄
2.2.14	SO ₂ Absorption in and Recovery From Methylammonium Sulfite-Bisulfite Solution
2.2.15	SO ₂ Absorption in and Recovery From a Xylidine-Water Mixture (Sulphidine Process)
2.2.16	Sodium-Barium Salt System for Absorption of SO ₂ and its Recovery as Sulfur
2.2.17	Sodium-Barium Salt System for Absorption and Recovery of SO ₂

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<u>Number</u>	<u>Name</u>
2.2.18	Absorption of SO_2 with Barium Hydroxide and its Recovery from BaSO_3 - BaSO_4
2.2.19	Absorption of SO_2 in $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and H_2SO_4 Liquid, and its Recovery From FeSO_4
2.2.20	Liquid Phase Oxidation of SO_2 with Ozone
2.2.21	Activated Charcoal Slurry Absorption and Recovery of SO_2
2.2.22	Absorption and Oxidation of SO_2 in Charcoal Beds (Sulfacid Process)
2.2.23	Adsorption and Recovery of SO_2 with Activated Char (Reinluft Process)
2.2.24	Adsorption of SO_2 with Dry Hydrated Lime with SO_2 Recovery by Calcination
2.2.25	Adsorption and Recovery of SO_2 with Silica-Alumina Alkali
2.2.26	Adsorption and Recovery of SO_2 with Alkalized Alumina
2.2.27	Adsorption of SO_2 with Dry Magnesia and Recovery from MgSO_3 - MgSO_4
2.2.28	Adsorption with Basic Aluminum Sulfate Solution, Regeneration with Heat to Release SO_2 (Hardman Holden)
2.2.29	Resin Adsorption of SO_2
2.2.30	Adsorption of SO_2 with a Molecular Sieve
2.3.1	Absorption of SO_2 with Acetic Acid Solubilized Limestone Slurry
2.3.2	Absorption of SO_2 in Limestone Slurry
2.3.3	Lime Absorption of SO_2
2.4.1	Absorption and Recovery of SO_2 and Production of Na_2SO_4
2.4.2	Absorption and Oxidation of SO_2 Producing MgSO_4 From MgO
2.4.3	Fulham Simon-Carves; Production of Sulfur and $(\text{NH}_4)_2\text{SO}_4$ From $(\text{NH}_4)_2\text{SO}_3$ - NH_4HSO_3 Solution

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<u>Number</u>	<u>Name</u>
2.4.4	Absorption of and Recovery of SO_2 Using $(\text{NH}_4)_2\text{SO}_3^-$ NH_4HSO_3 and H_2SO_4
2.4.5	Ammonium Sulfite-Bisulfite Absorption with SO_2 Recovery and NH_4NO_3 Production
2.4.6	Sulfuric Acid-Lime 2 Stage Absorption to Recover SO_2 and Produce Plaster of Paris
3.1.1	Dual Pad Mist Separator
3.1.2	Tubular Type Mist Separator
3.1.3	Panel Type Mist Separator
3.2.1	Electrostatic Precipitation
3.3.1	Mist Removal With Venturi Scrubber
3.4.1	Absorption and Neutralization of Acid Mist and SO_3 With Lime
4.1.1	Absorption of NO_x and SO_2 with Solid MgSO_3 and MgO
4.1.2	Reduction of NO_x and Absorption of SO_2 with Sulfite- Carbonate Solution
4.1.3	Absorption of SO_2 and NO_x with Sodium Hydroxide

In addition to these processes a study has been made of in plant process modifications which is included with SO_2 control systems under the designation 1.3.4.

On the process survey sheets which are included in the appendix we have used the terms "Licensor", "Expected Relative Cost" and "Reliability". The term "Licensor" is used to identify an organization which may have developed the process under consideration, and from whom it might be licensed. It does not imply that any formal licensing terms are available. Expected Relative Cost is a first impression estimate of the relative cost of any process with respect to others which have similar applications and capabilities. Reliability has to do with the effect of the process on the acid plant's on-stream capability, not necessarily the on-stream capability of the control system itself. For selected processes the on-stream factors are more fully discussed in IV-C and D.

B. FEASIBILITY AND APPLICABILITY CRITERIA

In order to measure the capabilities of various systems it is first necessary to establish criteria by which the various systems will be compared. For measurement of overall capability of a system or process we have used the term "control effectiveness", which may be defined as the total outlet concentration of sulfur expressed as ppm of SO_2 , regardless of the inlet concentration to the control system. For mist control only the measurement is normally given as mg/SCF.

Emission control systems were judged for feasibility by considering a number of factors including stage of process development, applicability to a significant number of existing acid plants, potential for good control effectiveness for SO_2 , acid mist or both, estimated on stream reliability, marketability of by-products (if any), and overall estimated value compared to other systems with similar chemistry or processing features. Those systems selected for further analysis were evaluated at SO_2 or overall control effectiveness levels of 2,000 ppm, 500 ppm, and 100 ppm or less. 2,000 is chosen since it represents the approximate level which can be achieved by most modern plants with careful operation and minimum expenditure. The 500 ppm level represents the present aim of many of the pollution control regulations presently under consideration in the United States. The 100 ppm level was chosen since it represents a desirable level below which SO_2 ceases to be much of a problem, or which may be the long-range requirement in the future.

The concentration of SO_2 in cleaned gas brings about concentrations of SO_2 in the ambient air at ground level in proportion to

the weight/unit of time being emitted from the stack. The contaminant concentration at ground level is also governed by distance from source to point of measurement, effective stack height, plus geographic and meteorological factors. The effective stack height and distance from source should be such that under the more unfavorable meteorological conditions the short durationed "peak" SO_2 concentrations should not exceed 1 ppm.⁽¹⁾ A stack emission of 100 ppm from most acid plants will generally result in an ambient air quality at ground level to satisfy this condition. For a specific plant the emission would have to be calculated using stack height and other local factors. A study of the effects of all the variables involved in the relationship between ground level concentration and stack emission level may be desirable.

Processes which control SO_2 emission may or may not provide a measure of control for acid mist as well. It is desirable to reduce acid mist emission to remove the visible plume from an acid plant stack. All such plants will discharge some acid mist to the atmosphere, and SO_3 will combine with the moisture in the air to form additional acid mist. Most devices presently used and which are incorporated on the stacks of many existing plants will remove nearly 100% of all mist particle of 3 microns or larger. The problem lies with that portion of the mist which is droplets of less than 3 microns. By removing all particles < 3 microns the mist emission can generally be reduced to 2-3 mg./SCF for plants producing up to 99% H_2SO_4 . For oleum plants, however, removal of particles < 3 microns reduces mist

(1) Whittenberger, James L. M.D. and Frank, Robert N. M.D.
"Human Exposures to Sulfur Dioxide" - Archives of
Environmental Health - Vol. 7, No. 2, August 1963

emission, but not nearly as effectively because the mist discharged from an oleum plant stack contains a much greater percentage of finer droplets, as discussed in Part III.

The relationship between the acid mist and SO_2 concentrations in the cleaned gas will be the same after dilution as at the stack, since mist particles are small enough to behave as a gas, especially in the smaller sizes. With the toxicity of acid mist at least 4 times as great as SO_2 ,⁽¹⁾ emissions of acid mist should be in the order of 3.0 mg/SCF (max.) (25 ppm) to avoid a contamination problem. This range was calculated using the same dispersion factors which are used to arrive at the SO_2 limit on the preceding page, and assuming that mist will behave in similar fashion. At these levels under some conditions there may still be some visible plume.

Selection of Processes for Further Study

In examining many processes we find that technically many have almost identical capabilities, requiring that further selection in many cases be based on other considerations. Among these considerations are:-

- . Processes which have reached a stage of development most closely approaching commercial operation receive favorable consideration, assuming that no limiting problems have been found.

(1) Ambient Air Quality Objectives - Classification System State of New York Air Pollution Control Board, Dec. 11, 1964

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- . Processes which produce a by-product which has a probable market in the U.S. are rated more feasible than processes which produce a by product for which the present supply far exceeds demand.
- . Processes which have application to many existing sulfuric acid plants are considered more feasible than those with limited applications.
- . Complex undeveloped processes are considered less feasible than simple undeveloped processes.
- . Processes which have toxicity problems, are obviously very expensive, which rely upon assumed technology with unknown capabilities are rated "not feasible", though at some later date further work may make some "feasible".
- . In comparing two very similar processes, for which it can be readily determined that one will have obvious cost advantages over the other, the more expensive has been rejected from further consideration in this study.

At least one "feasible" process has been selected from each sub-group of processes as described on page IV-2. "Feasible" as used here of necessity includes processes which are considered potentially feasible, assuming that the process as generally described will perform as expected. These generally apply to processes of the tail gas recovery group, in which very few of the processes have ever been used on a commercial scale. The only exception is chamber acid plants. This is discussed in IV-E.

C. SELECTED PROCESSES FOR SO₂ EMISSION CONTROL

Processes selected for more detailed review are grouped by control effectiveness on Tables 7, 8 and 9. Table 7 lists processes by identification number, which are for control of SO₂ to 100 ppm and below. The table also indicates if there are any limitations to the type or size of plant to which they may be applied, and what the concentration of SO₂ in the inlet gas would be to have a 100 ppm exit level.

Tables 8 and 9 present similar data for processes which can achieve 250 ppm and 500 ppm SO₂ emission levels. The intermediate level of 250 (Table 8) was added, as this is the level which can be reasonably achieved by most of the processes in Table 7 when applied to existing plants with the emission levels encountered when plants are older, and are pushed to their maximum production capability. These tables are based upon demonstrated absorption capabilities of 95-96% for most systems. 100 ppm control effectiveness might be achieved at increased SO₂ inlet concentrations by modification or additions to the absorption step.

The processes listed as having an optional capability for SO₃ and acid mist control are those which may or may not remove SO₃ and acid mist, depending upon the design of and pressure drop through the scrubber. The cost of this option is covered in Part V.

Following Table 9 each of the selected processes is described, and illustrated by process flow diagrams. These processes are arranged in numerical order and are as follows:

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- 1.1.1 Dual Absorption
- 1.2.1 Add-On Dual Absorption Using Converter Heat
- 1.2.2 Add-On Dual Absorption Using Furnace Heat
- 1.2.3 Add-On Dual Absorption Using Outside Heat Source
- 1.3.4 SO_2 - SO_3 Conversion Improvement
- 2.1.1 Na_2CO_3 Absorption of SO_2 to Produce Na_2SO_3
- 2.2.6 Magnesium Oxide Absorption of SO_2 with SO_2 Recovery
- 2.2.8 Potassium Sulfite-Bisulfite
- 2.2.14 SO_2 Absorption in and Recovery from Methylammonium Sulfite-Bisulfite Solution
- 2.2.22 Absorption and Oxidation of SO_2 in Charcoal Beds (Sulfacid Process)
- 2.2.28 Absorption with Basic Aluminum Sulfate Solution, Regeneration with Heat to Release SO_2 (Hardman-Holden)
- 2.2.29 Resin Adsorption of SO_2
- 2.3.3 Lime Absorption of SO_2
- 2.4.5 Ammonium Sulfite-Bisulfite Absorption with SO_2 Recovery and NH_4NO_3 Production
- 2.4.6 Sulfuric Acid-Lime 2 Stage Absorption to Recover SO_2 and Produce Plaster of Paris

It is recognized that several well developed processes have not been included in the above list for further study because they produce a by-product of which there is an overabundance. Notable in this group are several tail gas treating processes which use ammonia based scrubbing media, including 2.1.4, 2.4.3 and 2.4.4. One of these processes could very well be very attractive to a fertilizer producer who would have a natural market for a relatively small amount of $(\text{NH}_4)_2\text{SO}_4$ which could be used for blending in mixed fertilizers, for example. Process 2.4.4 would be quite similar to 2.4.5 which is reviewed, and which produces an ammonium nitrate by-product.

TABLE 7

FEASIBLE PROCESSES FOR
<100 PPM SO₂ CONTROL EFFECTIVENESS

<u>Process</u>	<u>Limitations of Application</u>	<u>SO₂ Inlet Concentration, ppm</u>	<u>Capable of SO₃ and Acid Mist Control</u>
2.1.1	None	2,500 or less *	optional
2.2.6	None	2,000 or less *	optional
2.2.8	None	2,000 or less *	yes
2.2.14	None	2,000 or less *	yes
2.2.29	None	None	yes
2.3.3	None	2,500 or less *	yes
2.4.5	None	2,000 or less *	yes
2.4.6	None	2,500 or less *	yes

* Based upon an expected capability in the Removal Section of 95 to 96%.

TABLE 8

FEASIBLE PROCESSES FOR
250 PPM SO₂ CONTROL EFFECTIVENESS

<u>Process</u>	<u>Limitations of Application</u>	<u>Limitation of SO₂ Inlet Concentration, ppm</u>	<u>Capable of Acid Mist and SO₃ Control</u>
2.1.1	None	6,000 or less *	optional
2.2.6	None	5,000 or less *	optional
2.2.8	None	5,000 or less *	yes
2.2.14	None	5,000 or less *	yes
2.2.22	None	2,800 or less **	yes
2.2.28	None	None	yes
2.2.29	None	None	yes
2.3.3	None	6,000 or less *	yes
2.4.5	None	5,000 or less *	yes
2.4.6	None	6,000 or less *	yes

* Based upon an expected capability in the Removal Section of 95 to 96%.

** Based upon a reported capability of about 90% removal.

TABLE 9
FEASIBLE PROCESSES FOR
500 PPM SO₂ CONTROL EFFECTIVENESS

<u>Process</u>	<u>Limitations of Application</u>	<u>Limitations of SO₂ Inlet Concentration, ppm</u>	<u>Capable of Acid Mist and SO₃ Control</u>
1.1.1	New S. Burning only	Not Applicable	No
1.2.1	Existing S. Burning only	None	No
1.2.2	Existing S. Burning only	None	No
1.2.3	Existing Wet Gas only	None	No
2.1.1	None	None	Optional
2.2.6	None	None	Optional
2.2.8	None	None	Yes
2.2.14	None	None	Yes
2.2.22	None	5,500 or less *	Yes
2.2.28	None	None	Yes
2.2.29	None	None	Yes
2.3.3	None	None	Yes
2.4.5	None	None	Yes
2.4.6	None	None	Yes

* Based on a reported capability of about 90% removal.

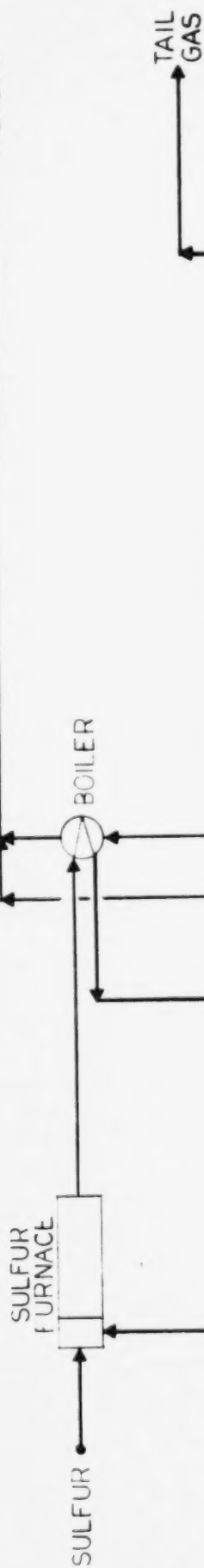
Dual Absorption (1.1.1)

In the dual absorption sulfuric acid plant pollution is reduced by converting a greater proportion of the sulfur dioxide in the feed to the converter to sulfuric acid and, in principle, this must be considered the best solution to the problem. It is, however, limited by theoretical considerations and below 500 ppm of SO_2 the catalyst loading and consequent power consumption will increase appreciably.

In a dual absorption plant, Figure 13, the SO_3 formed after partial conversion in two or three stages is removed in a primary absorption tower and the remainder of the gas, now with a very high O_2/SO_2 ratio is returned to the converter. A heat exchanger - or a series of exchangers reheats the gas from the absorber and cools the converted gas going to it. Because the O_2/SO_2 ratio in the partially absorbed gas is very high (at least 4:1 instead of 1.5:1) the equilibrium conversion is much higher and the second half of the converter with one or two stages of catalyst will ensure that at least 99.5% of the original SO_2 content of the gas is fully oxidized. This high potential conversion is not very much affected by the gas composition in the first part of the converter with the result that it is possible to operate these stages at a higher concentration of SO_2 than normal. This permits a reduction in equipment sizes which goes some way to cover the cost of the additional equipment required for the intermediate absorber stage.

The principle can be applied equally well to sulfur burning or wet gas plants. Typically a sulfur burning plant will operate at the 10-12% SO_2 level for dual absorption instead of the usual 8%. A wet gas plant will also operate at a higher SO_2 concentration than usual if this is

STEAM



PRIMARY
ABSORPTION
TOWER

BOILER

SECONDARY
ABSORPTION
TOWER

BOILER
FEED
WATER

DRYING
TOWER

AIR
BLOWER

COOLER

COOLER

COOLER

PRODUCT
ACID

LIST OF PARTS	
PART NO.	DESCRIPTION

CHEMICAL CONSTRUCTION CORPORATION
CONSULTING, DESIGNING AND CONTRACTING ENGINEERS
NEW YORK, N. Y. U.S.A.

SCHEMATIC FLOW DIAGRAM CONTROL METHOD I.1.1 DUAL ABSORPTION

THIS IS A REPRESENTATION OF A
SCHEMATIC FLOW DIAGRAM FOR THE
CONTROL METHOD I.1.1 DUAL ABSORPTION
PROCESS. IT IS NOT A PHYSICAL
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FIG.13

P

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DESIGNED	BY	DATE	DESIGNED	BY	DATE
DRAWN	BY	DATE	DRAWN	BY	DATE
CHECKED	BY	DATE	CHECKED	BY	DATE
APPROVED	BY	DATE	APPROVED	BY	DATE
REVIEWED	BY	DATE	REVIEWED	BY	DATE
REVISION	BY	DATE	REVISION	BY	DATE
REVISION	BY	DATE	REVISION	BY	DATE
REVISION	BY	DATE	REVISION	BY	DATE
REVISION	BY	DATE	REVISION	BY	DATE

available, as would normally be the case where H_2S , pyrites or spent acid was the raw material.

Because the wet gas dual absorption plant will contain two reheat cycles instead of one, it is sensitive to low gas strength and the principle is more difficult to apply to plants operating on a smelter gas where the available SO_2 is not under the control of the acid plant operator, than in the more self-contained pyrites, spent acid or sulfur based plants. For instance, if a plant is designed to operate on a copper converter gas varying cyclically between 3% and 8% SO_2 the converter stage, after the first absorption stage, will operate well at the 8% level, but when the concentration falls to 3%, practically all the conversion will take place in the primary stage, there will then be no heat generated in the secondary catalyst and the temperature will fall below the reaction point. When the gas strength recovers, it will be some time before the catalyst in this last stage becomes active and there will be a period of poor conversion. Although this problem could be mitigated by different arrangement of heat exchangers, it would probably be found necessary to use external heat in a converter preheater to maintain converter temperatures under proper control. It is doubtful if the advantages gained would be worth the trouble and expense entailed.

Except in these special cases, the dual absorption principle is a sound method of reducing air pollution and has the advantage of not introducing any new or unfamiliar techniques to the acid plant operator. Plants of this type have been operating in Germany and Holland for several years using both sulfur and roaster gas as feed. New plants using sulfur as feed are known to be under construction in the U.S., U.K., Japan and Australia, and some of these are now going into operation.

A dual absorption plant requires very little more plant area than a conventional single absorption plant. Although it includes an additional absorber and heat exchangers, the size of much of the equipment is somewhat smaller than the conventional plant. The dual absorption process includes no different types of equipment or additional unspared mechanical equipment, which means the on-stream factor should be unaffected and the plant should require no additional operators.

Dual absorption will generally provide a control effectiveness better than 500 ppm SO_2 . In itself it does not reduce the acid mist emission, thus a dual absorption plant will require the same type of mist control device as a conventional plant.

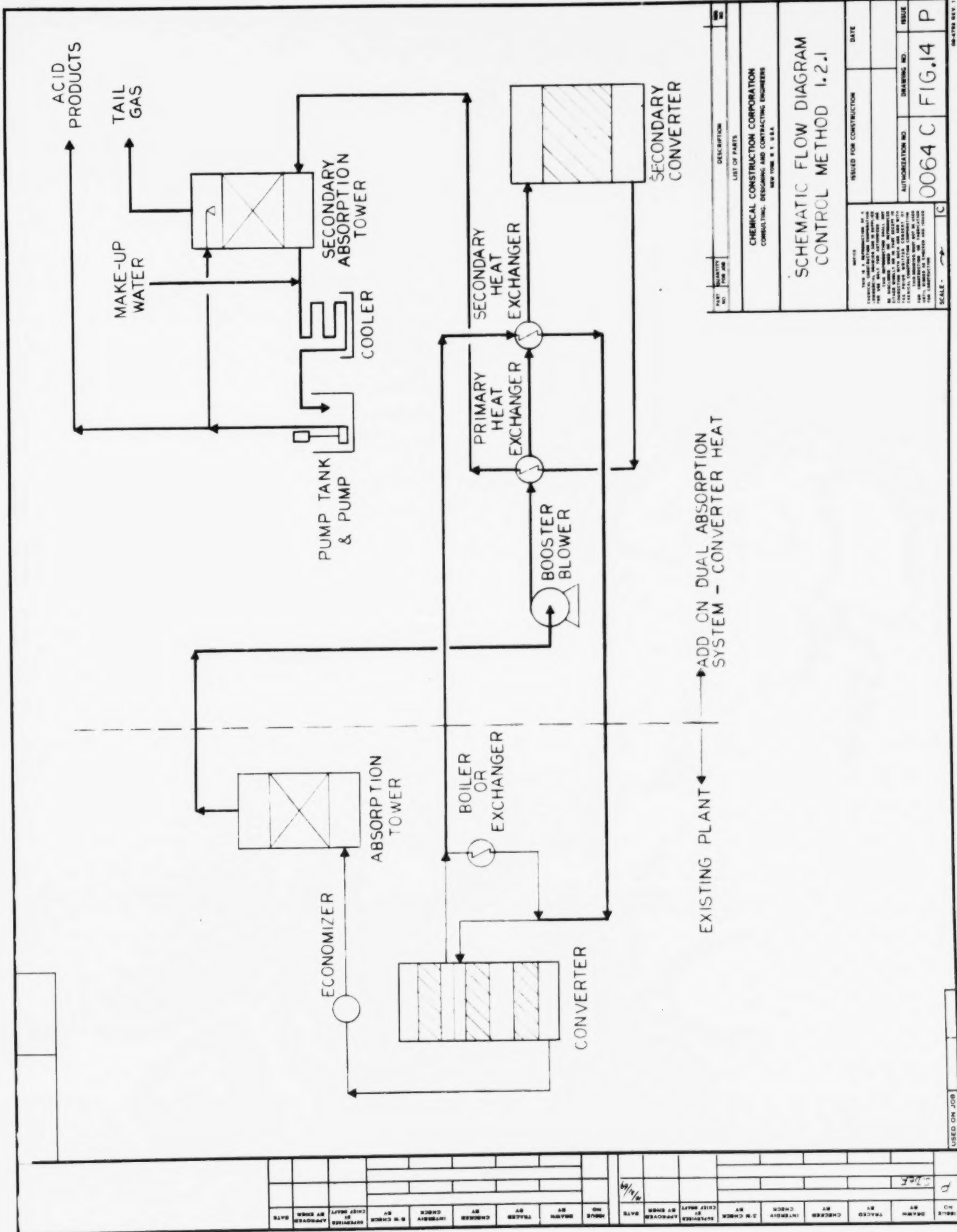
Add-On Dual Absorption Using Converter Heat (1.2.1)

The gas from the stack of the existing plant is pressurized by a blower and heated in a first heat exchanger by the gas leaving the secondary converter (see Figure 14). It is then further heated in a new heat exchanger installed in the base plant in parallel with the waste heat boiler or heat exchanger used to cool the gas after the first conversion stage. Dampers must be installed, if not already present, to restrict the flow through the existing boiler or exchanger to provide the heat required for the new one. Where the original plant has a converter boiler, the steam produced in it will be reduced. If it uses a heat exchanger, more gas must be by-passed around the burner gas boiler to make up for the heat taken by the new exchanger. In either case, the steam produced in the old plant will be reduced by 10 to 20%.

If the original plant includes a converter exchanger, this can be used for heating the new gas stream by making relatively simple piping changes. Although this saves the cost of a new exchanger, it takes more heat from the base plant than strictly necessary, resulting in a lower steam production so that the lower initial cost is balanced by a higher operating cost. In some cases, particularly where space is limited, this may be preferred.

It is desirable to locate the new converter and exchanger close to the original ones.

The converted gas from the secondary converter passes to the secondary absorption tower where the SO_3 formed is absorbed in 98.5% sulfuric acid. The absorber is furnished with the usual acid



EXISTING PLANT → ADD ON DUAL ABSORPTION SYSTEM - CONVERTER HEAT

PART NO.		DESCRIPTION	
LIST OF PARTS			
CHEMICAL CONSTRUCTION CORPORATION CONSULTING, DESIGNING AND CONTRACTING ENGINEERS NEW YORK, N. Y. U.S.A.			
SCHEMATIC FLOW DIAGRAM CONTROL METHOD 1.2.1			
ISSUED FOR CONSTRUCTION		DATE	
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0064 C		FIG. 14 P	
SCALE -		C	

circulation and cooling system which should be connected to the circulation system of the base plant so that the acid concentration can be controlled and the product removed. Tail gas is exhausted to the atmosphere from the absorption tower, and in most cases the process can be designed so that the SO_2 emission will not exceed 500 ppm SO_2 .

The process has advantages in addition to reducing SO_2 emissions. SO_2 being wasted will be converted to product acid. It may be possible to increase the SO_2 concentration in the base plant and so increase production. The increase in concentration will cause decreased conversion in the base plant which is then recovered in the secondary system. This will permit the additional operating cost to be distributed over a larger production tonnage, reducing somewhat the increased cost per ton without exceeding a 500 ppm emission.

The process is not affected by the present plant emission level, but, as shown in Part V, the control cost is lower when the process is applied to the less efficient plant.

The space required for the additional equipment for this process is about 2,500 sq. ft. for a 250 T/D conventional plant. The space should be located near to the existing converter and absorber. The acid coolers should be added adjacent to the existing ones to avoid additional water piping. This space may be difficult to find in some plants which have been surrounded by a chemical complex. Additionally, some equipment will probably require field erection which means access must be available for heavy construction equipment. In order to tie-in the new equipment, a longer than normal acid plant shut down will probably be necessary.

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As with a new dual absorption plant, process 1.2.1 will provide a control effectiveness of ≤ 500 ppm SO_2 , and will not affect acid mist emission.

Since this process will reduce acid plant steam production, a complex which is "tight" on steam may have to provide an alternate steam or heat source.

Process 1.2.1 should have a high on stream factor, since it adds only one centrifugal type blower to the mechanical equipment, (acid pumps are normally spared) but the overall onstream factor may be slightly reduced, perhaps 1%. No additional operators should be required.

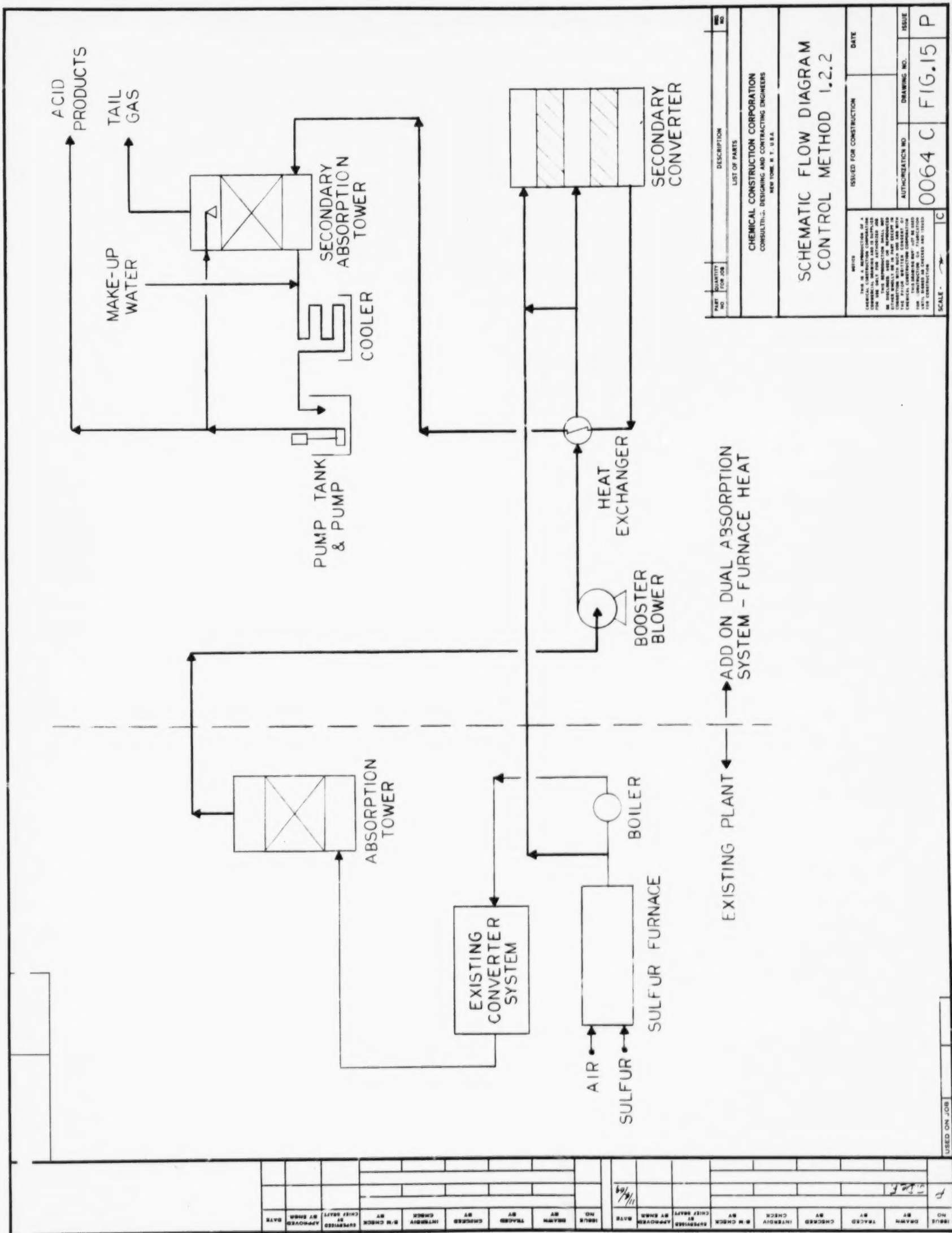
Add on dual absorption (process 1.2.1 and 1.2.2) are being offered commercially, although none have been built as yet. They represent no real departure from current sulfuric acid design or technology.

Add-On Dual Absorption Using Furnace Heat (1.2.2)

The stack gas from the base plant is pressurized by a blower and partially heated by the gas leaving the secondary converter. (Figure 15) The additional heat to bring it up to reaction temperature is then obtained by mixing - with the stack gas - hot burner gas from the sulfur furnace of the base plant. As the gas will be at a temperature of $1,600^{\circ}\text{F}$ to $1,900^{\circ}\text{F}$, only a small quantity will be required to heat the tail gas from 700°F to 800°F . Because this gas contains 10 to 12% SO_2 which bypasses the first converter system, a two stage converter is required to give conversion equivalent to process 1.2.1. The control of the temperature of the second stage is obtained by mixing the partially converted gas with a proportion of the 700°F tail gas from the first heat exchanger.

The converted gas from the secondary converter passes to the secondary absorption tower where the SO_3 formed is absorbed in 98.5% sulfuric acid. The absorber is equipped with the usual acid circulation and cooler system and this is connected to the circulation system of the base plant so that the acid concentration can be controlled and the product removed. Tail gas is exhausted to the atmosphere from the absorption tower outlet and, in most cases, this gas contains less than 500 ppm of SO_2 .

In addition to the advantages cited for process 1.2.1, this system can produce additional acid from the additional sulfur burned to provide heat for the second converter. The quantity is limited only by the capacity of the main blower and the sulfur furnace. Additional modifications to the heat exchange system could increase plant capacity by as much as 35%.



NO.	DATE	DESCRIPTION	NO.
LIST OF PARTS			
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SCHEMATIC FLOW DIAGRAM CONTROL METHOD 1.2.2			
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0064 C		FIG. 15 P	
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The drawbacks of process 1.2.2 are the same as those cited for process 1.2.1. The additional space requirements, the on stream reliability and operator requirements are also the same as for process 1.2.1.

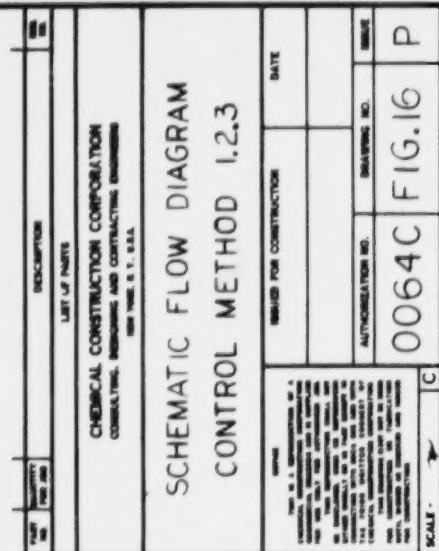
Add-On Dual Absorption Using Outside Heat Source (1.2.3)

This process is essentially the same as process 1.2.1 (see Figure 16) except that the heat for raising the temperature of the gas leaving the primary absorber to the proper temperature for introduction into the secondary converter is provided from an outside heat source by burning fuel oil or natural gas. This is necessary in a wet gas plant in which there is no excess heat available, such as a plant operating on smelter gas. With other types of wet gas plants, though heat gas would be available, as from a sludge furnace, the SO_2 would be wet and not suitable for introduction into the converter as in process 1.2.2.

This process can achieve the same result as 1.2.1 and 1.2.2 for wet gas plants, but at an obviously greater expense because of fuel requirements. It is possible that a special situation might exist where an outside waste heat source adjacent to a wet gas plant could be utilized to permit an installation like 1.2.1, with no cost heat, but this is remote.

The on stream factor will be slightly lower than 1.2.1 and 1.2.1 due to the furnace and fuel supply required. Additional operator attention probably would not be required since "wet gas" plants generally have more operators than a sulfur burner, being more complex.

Space requirements for 1.2.3 would be about 3,500 sq. ft. for a 250 T/D plant, since wet gas plants, due to generally lower gas strengths, have larger equipment than sulfur burners. This space may be difficult to find around a sludge or H_2S burning plant, or a smelter gas plant.

[illegible]

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This process will have all the problems of access to construction space, shutdown for installation, and limitations as described for process 1.2.1. It will, similarly, provide no additional acid mist control. There is no possibility of greatly increased production with smelter gas plants since the sulfur supply is not controlled by the acid plant operator.

SO₂-SO₃ Conversion Improvement (1.3.4)

Probably the easiest method to reduce SO₂ emission levels from existing plants is to improve SO₂ conversion by modifying the parameters which control the SO₂ oxidation reaction. These parameters are:-

- (1) Catalyst quantity and activity
- (2) Reaction gas composition
- (3) Reaction gas temperature
- (4) Residence time
- (5) Removal of reaction products

The discussion that follows will deal exclusively with the conversion improvement of existing single absorption H₂SO₄ plants by means of items 1 through 4 listed above. Item 5 deals with dual absorption and has already been discussed.

Possible in-plant modifications are:-

- (1) Addition of extra catalyst to one or more beds of existing catalyst in the converter, or complete catalyst replacement.
- (2) Lower the SO₂/O₂ ratio by the addition of oxygen or air to the reaction gas either prior to the first catalytic stage or later at any intermediate stage.
- (3) Lower the feed temperature of the reaction gas. In most cases this will necessitate replacing the existing catalyst with low temperature catalyst.
- (4) Increase the residence time either by installing a new converter in parallel with the existing one or by reducing reaction gas throughput, i. e., reducing plant capacity. In

this study the installation of a new converter will be ignored because of the special nature of such a venture, subject to space limitations, revamp of duct work, etc. On the other hand, most sulfuric plants are operated at a higher capacity than design at the expense of higher SO₂ emissions.

The modification of a specific plant may involve the adoption of any one improvement method or a combination of all four. Due to the wide divergence of design parameters and operation of existing converters, when discussing possible modifications an improvement limitation approach has been taken, rather than proposing a specific modification scheme for a class of converters. In the future, when implementing these modifications, each case must be studied on its own merits.

The practical aspects of the theoretical limitations discussed in Part III-A are as follows:

Catalyst Addition

Usually only 3-6 inches of additional bed height is available per stage. Air quench type converters are expected to have more room for catalyst addition.

Air Addition

Fan capacity is the most important limiting factor. Existing air dryers and associated equipment should be able to handle extra air within limits, heat exchangers likewise. In general, existing equipment should be able to handle a 10-15% increase over design air rates. Table 10 lists relative air requirements for feed gas concentrations of 4% to 12%

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TABLE 10

RELATIVE AIR REQUIREMENTS

BASIS 8% SO₂ FEED AIR = 1.0

<u>% SO₂</u>	<u>Air Rate Factor</u>
4	2.000
5	1.600
6	1.334
7	1.143
8	1.000
9	0.889
10	0.800
11	0.727
12	0.666

SO₂. The tight water balance of an oleum plant may require the additional air to be predried in equipment other than the drying tower.

Feed Temperature Reduction

As discussed earlier this is useful only at the final conversion stage, the existing catalyst has to be replaced by low temperature catalyst and intercoolers preceding the stage may be easily altered for extra heat exchange.

In some cases a higher capacity cooling air fan may be required.

Reduced Production

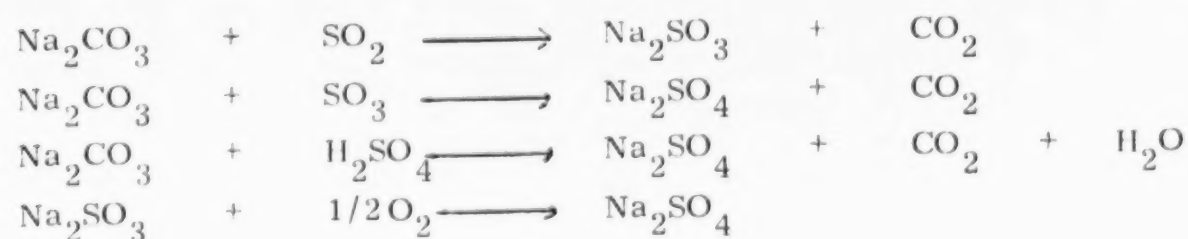
As discussed in Part III-A, conversion may be improved by burning less sulfur, with or without reduction in air flow. This is a costly, but sometimes necessary way to temporarily reduce emission during adverse atmospheric conditions. Most plants can probably operate at 50 to 60% of capacity with improved conversion, and still maintain proper reaction temperature in the converter. A minimum temperature is especially important in the last stage, where if the reaction is insufficient to offset heat losses, higher SO₂ emission will result.

It can be seen from Figure 3 that it is all but impossible to achieve anything near 500 ppm emission level with any or all of the modifications discussed above. Nevertheless, these are completely feasible approaches to achieve some reduction in SO₂ emission levels. These modifications require minimum capital cost, little or no additional space and no additional plant personnel. The improvement may be marginal, but where a plant is operating just outside acceptable standards the methods discussed here should be carefully considered.

Sodium Carbonate Absorption of SO₂ to Produce Sodium Sulfite (2.1.1)

The objective of this process is to produce a salable sodium sulfite from sodium carbonate and the SO₂ in the acid plant tail gas, reducing the total emission level of sulfur dioxide from 2,000 ppm to as low as 100 ppm. This process is not in commercial operation, although a considerable amount of development work has been done. Since the process requires low pressure steam which is often available in excess from H₂SO₄ plants, this process is considered potentially feasible. Na₂SO₃ should find a market, possibly in the paper industry.

Sulfur dioxide, SO₂ and acid mist are removed in a single-stage venturi type scrubber (Figure 17). The scrubbing liquid is primarily a solution of sodium sulfite with smaller amounts of sodium sulfate and carbonate. SO₂ is absorbed into the scrubbing liquid, it then reacts with the sodium carbonate to form sodium sulfite. Some of the sulfite is oxidized to sulfate. The acid mist and SO₃ are removed from the gas stream by entrainment in the absorbing solution in the throat of the scrubber. Any SO₃ is converted to acid mist. Since the single scrubber would be primarily designed for SO₂ absorption, removal efficiency for acid mist may not reach the optimum. The entrained acid and trioxide react with the alkali to form sodium sulfate. The reactions are as follows:



Sodium carbonate is brought into the system dissolved in the required make-up water. An oxidation inhibitor is added in small amounts to minimize oxidation of the sulfite to sulfate.

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A bleed stream is drawn from the scrubber stream to process the sodium sulfite. The solution is first cooled to about 35⁰F in a steam-jet vacuum crystallizer. Hydrated sulfite and sulfate are precipitated and a slurry of this material is centrifuged. Supernatant liquids are returned to the scrubber. The hydrated crystals are then heated (to 110⁰F) in a second crystallizer forming a slurry of anhydrous salts. These salts are centrifuged, and then dried at 250+⁰F in a rotary dryer fired with natural gas. The dried salt is then ground and sent to storage.

Processing problems may be encountered in preventing oxidation of sulfite to sulfate in the scrubber and other parts of the system to maintain a minimum percentage of sulfite in the product. A suitable oxidation inhibitor would have to be selected. The ease with which sodium sulfite is precipitated in the low and high temperature crystallizers must also be determined.

The complexity of the process will require the attention of a full time operator plus a second on a part time basis for handling of the by-product.

Space requirements for process 2.1.1 for a 250 T/D sulfur burning plant would be approximately 2,500 sq. ft., none of which need be inside the acid plant battery limits. The scrubber would need to be located adjacent to the acid plant, but the remainder of the system could be some distance away, with the bleed stream being piped to it and makeup Na_2CO_3 returned. Only two small lines are required.

Since the recovery process is not integral with the acid plant it in no way will affect the on-stream factor of the acid unit. Should it be

shut down the scrubber would operate until the holding tank was filled. If the 2.1.1 process were still not operating, SO_2 would have to be temporarily vented to atmosphere. Process 2.1.1, having a relatively large number of mechanical items probably would have a lower on-stream factor than the associated H_2SO_4 unit.

The number of potential users is rather limited by the by-product Na_2SO_3 . The largest potential market is in kraft pulp mills which presently buy Na_2SO_4 . The sulfite, if available, would provide the same Na and S values in a smaller tonnage for mixing with black liquor, the ultimate need in the kraft process being for Na_2S . Since the location of kraft mills is limited geographically, the acid plants with potential applications for process 2.1.1 would be those in reasonable proximity to kraft pulp mills. Many kraft mills, of course, are located in the southeastern states as are many acid plants.

An acid plant pushed to maximum capacity with process 2.1.1 as a control system will produce additional sodium sulfite, as well as additional H_2SO_4 . This may be a disadvantage, depending upon the Na_2SO_3 market. A 250 T/D H_2SO_4 plant with a 4,000 ppm emission level would produce approximately 15.5 T/D of dry Na_2SO_3 including some Na_2SO_4 and Na_2CO_3 which are tolerable for the suggested end use.

As with many other tailgas treatment processes, the control effectiveness of the process is affected by the inlet SO_2 concentration. With a 95% removal, the control level can be 250 ppm with an inlet concentration of 5,000 ppm, and 100 with an inlet SO_2 concentration of 2,000.

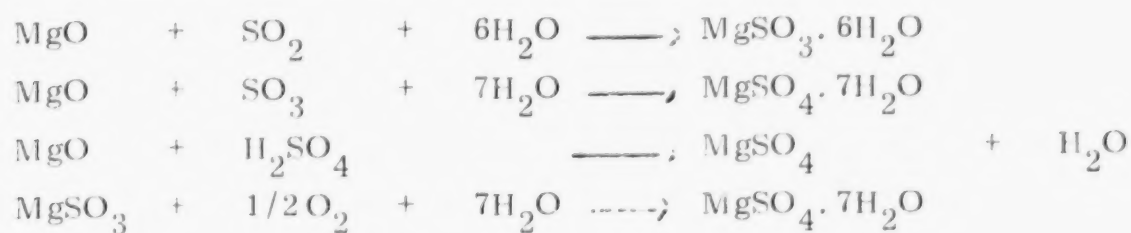
A greater removal than 95% is possible by changing the composition of the scrubbing liquid or adding absorption stages.

Magnesium Oxide Absorption of SO₂ With SO₂ Recovery (2.2.6)

The objective of this process, illustrated by Figure 18, is to absorb SO₂ in a magnesium oxide-sulfite water slurry and then calcine the magnesium sulfite to recover the SO₂ and the magnesium oxide.

The process can reduce the sulfur emission level, for example, from 2,000 ppm to about 100 ppm. Although this system is not yet in commercial operation, it has operated successfully in pilot scale on a sulfuric acid plant, and commercial scale units have been proposed.

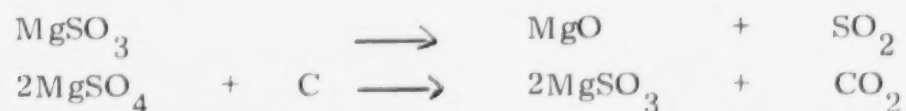
The SO₂, SO₃ and acid mist are removed from the tail gas in a single-stage venturi type scrubber. SO₂ is absorbed into the slurry, reacting with the magnesium oxide to form magnesium sulfite. Acid mist and SO₃ are removed by entrainment in the scrubber. In similarity to process 2.1.1 acid mist removal efficiency would have to be ascertained. The SO₃ and H₂SO₄ combines with the oxide to form magnesium sulfate. Some magnesium sulfite is oxidized to sulfate by the oxygen in the tail gas. The chemical reactions are as follows:



A bleed stream of the slurry is processed to recover the SO₂ and regenerate the magnesium oxide absorbant. The slurry is first centrifuged to remove most of the free water. The wetted solids are then dried in an oil-fired rotary dryer to remove the free water as well as the waters of hydration. Following the drying the salts are

[illegible]

calcined, decomposing to SO_2 and magnesium oxide. Coke is added to reduce magnesium sulfate to sulfite:-



The calciner can be either oil or gas-fired and the off-gases containing the SO_2 and some MgO dust are passed through a cyclone to remove most of the dust, and then through a scrubber for a final cleaning. The scrubbing liquid is magnesium bisulfite. The gases are then indirectly cooled to condense most of the moisture. Following this they are compressed to atmospheric pressure before being returned to the acid plant.

The calcined material, MgO , is sent to the slurry tank where it is slurried with the required make-up water for return to the scrubber system. Magnesium oxide make-up is also added to the slurry tank. The magnesium bisulfite bleed stream from the calciner dust scrubber is sent to the SO_2 absorber.

The control effectiveness of this process is affected by inlet SO_2 concentration. Tests have demonstrated that 95% of the SO_2 can be removed in the scrubber. At constant SO_2 concentration the cost of controlling to 200 ppm is insignificantly higher than controlling to 500 ppm. If SO_2 concentration increases the exit SO_2 concentration can be maintained by adding more alkali to the absorbing slurry.

The physical space requirements for process 2.2.6 for application to a 250 T/D H_2SO_4 plant is about 2,000 sq. ft. The entire unit should be located adjacent to the acid plant, but not necessarily within the

battery limit. Being adjacent to it will permit a short duct for return of SO_2 to the drying tower.

Mechanical equipment will tend to reduce the on stream factor of the process below that of the acid plant, and will also require the attention of a full time operator. Since the system is independent of the acid plant it will not affect operation of the acid plant, but will mean SO_2 is vented to atmosphere when the recovery process is not operating.

Since the product of this system is SO_2 , operation of the acid plant above design levels when using process 2.2.6 can permit a substantial increase in acid production while keeping SO_2 emissions below 500 ppm.

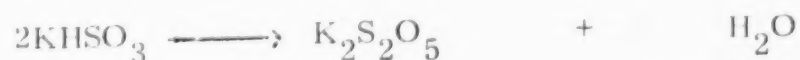
Potassium Sulfite-Bisulfite (2.2.8)

This process is basically of the type developed by Wellman-Lord for absorption of SO_2 with a potassium sulfite-bisulfite solution, which is subsequently heated to liberate SO_2 . The process has been piloted, and a commercial scale unit is being constructed. A version of this type of process is illustrated by Figure 19.

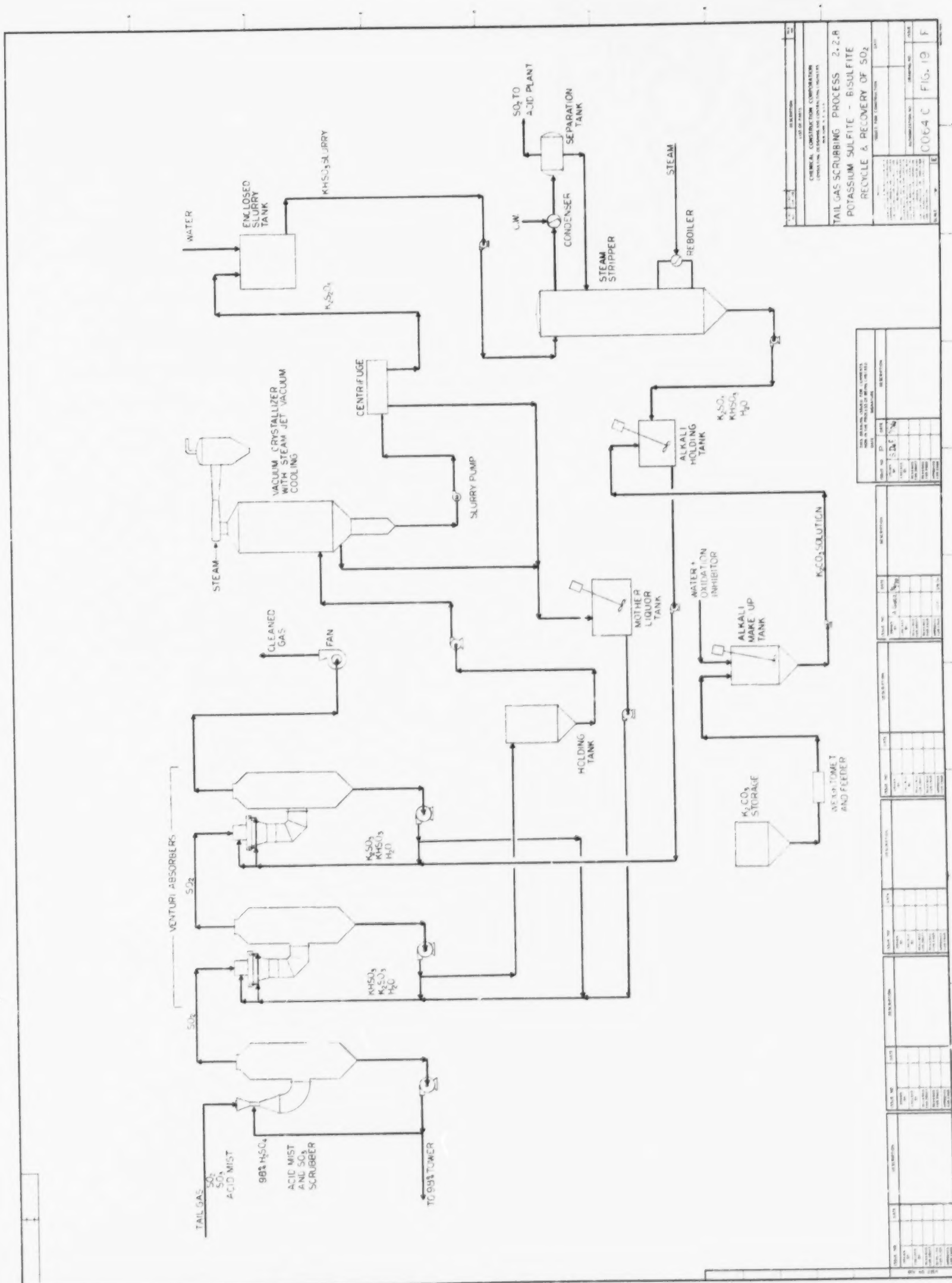
The tail gases are first scrubbed in a high pressure drop venturi with a sulfuric acid solution to remove acid mist and SO_3 . Depending upon inlet concentrations, very high removal efficiencies can be obtained (in the order of 99%). Following this, the SO_2 is absorbed in two stages with potassium sulfite-bisulfite solutions. A solution stronger in bisulfite in the first stage (higher permissible SO_2 vapor pressure) is bled to the regeneration part of the system. An oxidation inhibitor is added to minimize oxidation of sulfite to sulfate. The absorption chemistry is as follows:



The sulfite-bisulfite bleed stream is first cooled to about 40°F to precipitate potassium pyrosulfite:



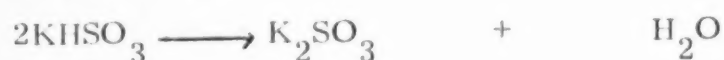
This is done to concentrate the SO_2 recoverable material to a maximum. The pyrosulfite crystals are separated by centrifuging. Water is then added to the crystals to form a bisulfite-pyrosulfite slurry which is fed into the steam stripper.



REVISIONS		DATE		BY	
1	AS SHOWN	10/1/68	W. J. H.	W. J. H.	W. J. H.
CHEMICAL CONSTRUCTION CORPORATION 1000 LEXINGTON AVENUE, NEW YORK 17, N.Y.					
TAIL GAS SCRUBBING PROCESS - 2.2.B POTASSIUM SULFITE - BISULFITE RECYCLE & RECOVERY OF SO_2					
SHEET NO.		SHEET TOTAL		FIG. 19	
0064 C		F		F	

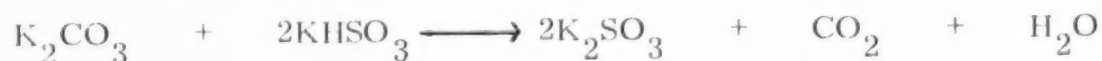
ITEM NO.	DESCRIPTION	QTY.	UNIT	REMARKS
1	VENTURI ABSORBERS	1	EA	
2	98% H_2SO_4 ACID MIST AND SO_2 SCRUBBER	1	EA	
3	TOBNA TOWER	1	EA	
4	HOLDING TANK	1	EA	
5	MOTHER LIQUOR TANK	1	EA	
6	CENTRIFUGE	1	EA	
7	VACUUM CRYSTALLIZER WITH STEAM JET VACUUM COOLING	1	EA	
8	ENCLOSED SLURRY TANK	1	EA	
9	SEPARATION TANK	1	EA	
10	STEAM STRIPPER	1	EA	
11	REBOILER	1	EA	
12	CONDENSER	1	EA	
13	ALKALI HOLDING TANK	1	EA	
14	ALKALI MAKE UP TANK	1	EA	
15	K_2CO_3 STORAGE	1	EA	
16	WATER + OXIDATION INHIBITOR	1	EA	
17	SLURRY PUMP	1	EA	
18	FAN	1	EA	
19	STEAM	1	EA	
20	WATER	1	EA	
21	SO_2 TO ACID PLANT	1	EA	

In the steam stripper, the bisulfite-pyrosulfite slurry is indirectly heated to about 250°F with steam from the acid plant. The pyrosulfite crystals dissolve to form bisulfite and the latter decomposes to sulfite and SO₂:



The overhead gas is a saturated steam-SO₂ mixture which is passed through a water-cooled condenser where the mixture is indirectly cooled to about 110°F. The condensate, a saturated SO₂ solution, is returned to the stripper, and the cooled, highly concentrated SO₂ gas is cycled to the acid plant.

The decomposed solution containing potassium sulfite with a smaller amount of bisulfite is mixed with the alkali and water make-up before it is cycled to the second absorption stage. The alkali reacts as follows:



Some areas of this process which may require further development involve the absorption efficiencies of SO₂ in both stages as related to bisulfite-sulfite concentrations. Also, the temperature-time-recycle-percent precipitation relationships of the crystallization of potassium pyrosulfite need to be fully determined. The steam consumption in the stripping of the bisulfite-pyrosulfite slurry and the percent bisulfite decomposition need verification, all by continuous operation on a commercial scale. Since complete information has not been released on the details of the process, some of this information may already be developed.

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It would be desirable to find an oxidation inhibitor to minimize oxidation of sulfite to sulfate if this is not presently done. The sulfate is not readily regenerated to sulfite for recirculation, and sulfate buildup would gradually render the process ineffective.

The equipment required for the version of this process illustrated in Figure 19 is mainly vessels handling gases and liquids with a minimum of mechanical equipment which should give an on stream factor similar to that which is expected of a contact acid plant. Since it operates independently of the acid plant, process 2.2.8, when not operating, would vent acid plant tail gas to atmosphere as at present. Multiple scrubbers, crystallizer, centrifuge and make-up tanks will require a full time operator for the process.

The small amount of weak acid from the mist scrubbing stage can be cycled to the acid plant.

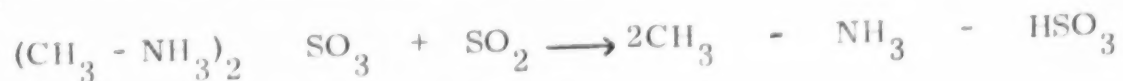
About 2,000 square feet would be required for the illustrated system adjacent to a 250 T/D acid plant for the same reasons as described for process 2.2.6.

SO₂ Absorption in and Recovery from Methylammonium Sulfite-Bisulfite Solution (2.2.14)

This process to control SO₂, SO₃ and acid mist at a control effectiveness as low as 100 ppm and recover SO₂ for recycle to the acid plant has not been operated commercially, but is included for its apparent potential as a feasible process and is illustrated by Figure 20.

SO₂ is absorbed in two counter-current absorption towers with methylammonium sulfite-bisulfite solutions. The bleed streams are then heated in a steam stripper, releasing SO₂ for recycle to the acid plant, with the bisulfite being converted to sulfite. The absorbing solutions are prepared from liquid methylamine and sulfur dioxide.

SO₂ is absorbed with the following reaction taking place:-



The concentrations of bisulfite and sulfite were carefully calculated to keep SO₂ and methylamine vapor pressures sufficiently low to have the required absorption of SO₂ with minimal evolution of methylamine vapor. (There is a vapor pressure of methylamine even though it exists in the combined state with SO₂.) At the absorption temperatures the vapor pressure of methylamine is quite low.

Bleed streams from the two absorption towers are fed into a steam stripper where the incoming liquid is preheated in two stages; first by the existing liquid and then by 50 pound steam from the acid plant. The liquid in the tower is heated indirectly by 50 pound steam. The rich liquid is stripped by the rising vapor mixture and methylamine vapor

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is condensed by a reflux stream from a partial condenser. The exiting SO_2 gases are cooled indirectly with the removal of most of the water.

The stripper bottoms containing methylammonium sulfite and water are recycled to the absorption towers. Make-up to the system is in the form of methylamine sulfite and is prepared in the same fashion as the absorbing solutions.

Since this process has not been developed it has several potential problems, which must be resolved. There may be difficulty in preparing large quantities of methylammonium sulfite-bisulfite for initial operations because of the volatility and flammability of methylamine. The extent of oxidation of the solution to methylamine sulfate in the absorption and stripping stages is unknown. Johnstone specified hydroquinone as an oxidation inhibitor, but this should be confirmed with pilot tests.

The control effectiveness can be varied by changing the size of the absorption towers. Mist is removed as with process 2.2.8.

This potentially feasible process should be relatively simple to operate with the part time attention of an operator. Being a gas-liquid system with no complex mechanical equipment it should have a high on stream factor, as good or better than a contact acid plant. Like other tail gas treating systems, 2.2.14 operates independently of the H_2SO_4 plant to which it is applied.

A unit for tail gas emission control on a 250 T/D sulfuric acid plant would require about 2,000 square feet adjacent to the acid plant.

Absorption and Oxidation of SO_2 in Charcoal Beds (Sulfacid Process) (2.2.22)

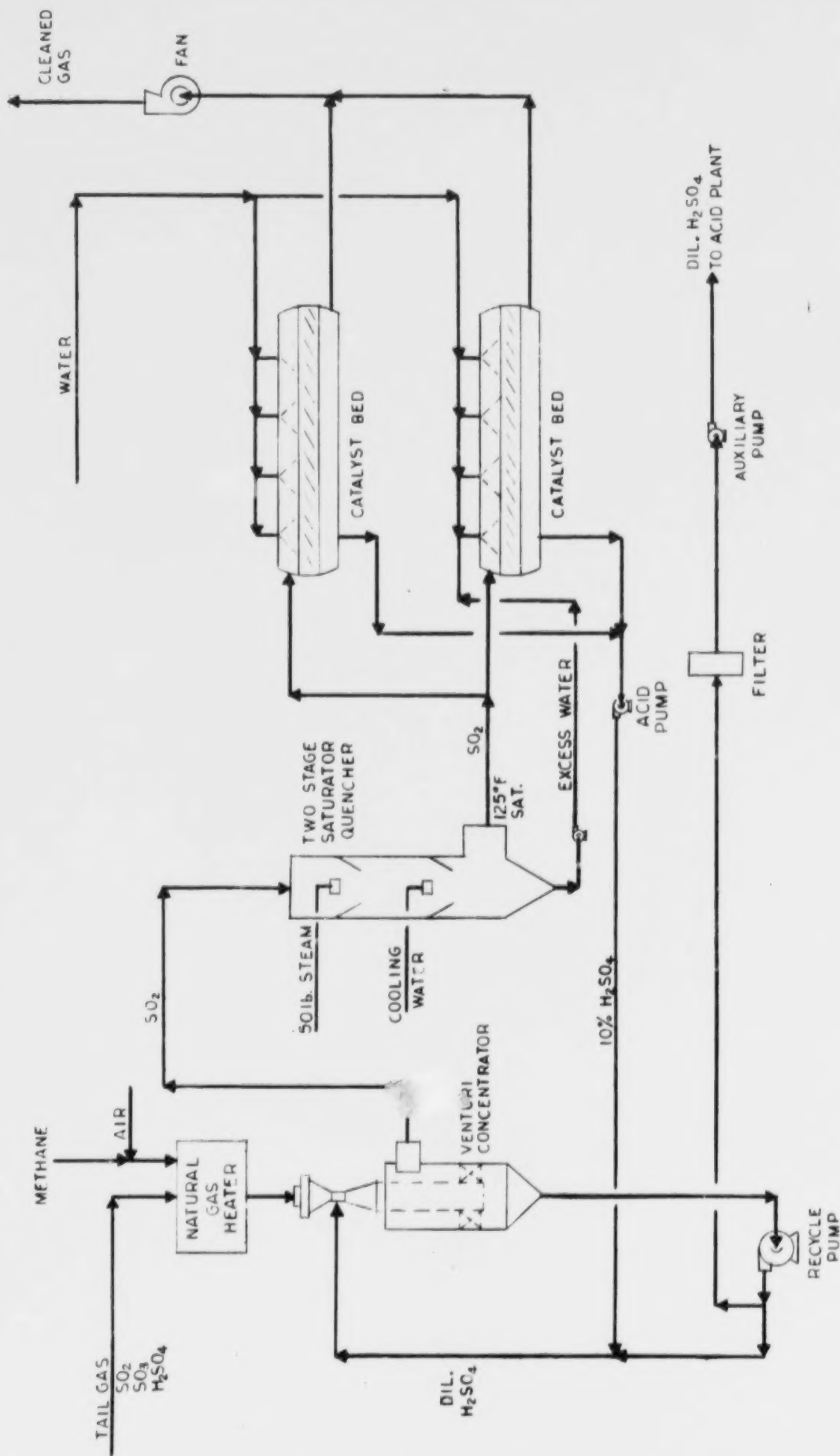
This process, as illustrated by Figure 21, has been modified to satisfy acid plant conditions over a range of SO_2 concentrations in tail gas from 3,000 to 833 ppm, equivalent to acid plant efficiencies from 96% to 99%.

This process, which is in commercial operation in Europe, catalytically oxidizes SO_2 to dilute sulfuric acid and then concentrates the acid to the point at which it may be recycled to the acid plant without upsetting the plant water balance. Concentration is achieved in a venturi type scrubber by saturating the tail gas. Supplementary heat is added upstream of the scrubber to achieve more evaporation at lower acid plant efficiencies.

The sulfacid process in its present stage of development employs activated carbon to catalytically oxidize 95% (in this example) of the SO_2 to form a 10% H_2SO_4 . Gas velocity through the catalyst bed is quite low, in the order of 0.33 feet per second.

The degree of concentration required for acid produced by the sulfacid process depends upon several factors, including existing acid plant conversion efficiency, the grades of product acid being produced and the humidity of the air entering the plant via the drying tower.

It can be seen from Table 11 that at a plant efficiency of 99% or better (with humidity and product grade fixed) all of the 10% acid can be assimilated by the acid plant without evaporation supplementary heat being required. Between 98 and 99% the 10% acid must be concentrated in the scrubber before recycle to the acid plant. Below the 98% level supplementary heat is required and this may be provided by direct firing in the duct upstream of the venturi, enabling additional water to be



PART NO.		DESCRIPTION	LIST OF PARTS
CHEMICAL CONSTRUCTION CORPORATION CONSULTING, DESIGNING AND CONTRACTING ENGINEERS NEW YORK, N. Y. U.S.A.			
TAIL GAS SCRUBBING PROCESS 2.2.22 CATALYTIC CONVERSION OF SO_2 & WATER TO DILUTE H_2SO_4 SULFACID PROCESS			
ISSUED FOR CONSTRUCTION		DATE	
AUTHORIZATION NO.		DRAWING NO.	
0064 C		FIG 21	
SCALE		REV. 1	

1.1	DESIGNED BY	1.2	1/1/54
2.1	CHECKED BY	2.2	1/1/54
3.1	APPROVED BY	3.2	1/1/54
4.1	REVIEWED BY	4.2	1/1/54
5.1	DESIGNED BY	5.2	1/1/54
6.1	CHECKED BY	6.2	1/1/54
7.1	APPROVED BY	7.2	1/1/54
8.1	REVIEWED BY	8.2	1/1/54
9.1	DESIGNED BY	9.2	1/1/54
10.1	CHECKED BY	10.2	1/1/54
11.1	APPROVED BY	11.2	1/1/54
12.1	REVIEWED BY	12.2	1/1/54
13.1	DESIGNED BY	13.2	1/1/54
14.1	CHECKED BY	14.2	1/1/54
15.1	APPROVED BY	15.2	1/1/54
16.1	REVIEWED BY	16.2	1/1/54
17.1	DESIGNED BY	17.2	1/1/54
18.1	CHECKED BY	18.2	1/1/54
19.1	APPROVED BY	19.2	1/1/54
20.1	REVIEWED BY	20.2	1/1/54

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evaporated in the venturi concentrator.

In addition to water limitations, the tail gas entering the catalyst bed must be saturated to a minimum temperature of 125⁰F. This requirement may be met by injecting low pressure steam and some water downstream of the concentrator in a 2-stage quencher. Steam and water saturation are required for plants 96% and over in efficiency. With less efficient plants the tail gases would be heated to the point where concentration alone would produce a saturated gas at 125⁰F.

Further development work is being carried on by Lurgi to raise the concentration of the dilute 10% acid now produced. If successful this should substantially reduce one of the major technical drawbacks of the process in its present form.

The necessity for using supplementary heat to concentrate the product to usable form is a serious economic drawback. The alternative to adding heat would be to neutralize and dispose of surplus dilute acid - an undesirable prospect. When large gas volumes or gases with high SO₂ concentrations must be handled structural problems arise in the reactor design in connection with support of the catalyst bed. This point may or may not be reached if a Sulfacid unit were designed for a very large acid plant or one with a high emission level.

While most other tail gas recovery processes will handle increased SO₂ loading resulting from plant operation in excess of design capacity with improved economics, the Sulfacid process in its present form would offer no advantage in this area. Control effectiveness is limited by inlet SO₂ level as well as gas volume.

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The Sulfacid process also has some distinct advantages, probably the most important being that it is in actual commercial operation. In addition, it is a relatively simple process with only minor mechanical equipment which should give it a high on-stream factor.

In addition to increasing product acid strength, development of a catalyst which would permit the oxidation in the reactor to be achieved at higher gas velocities would improve the process.

TABLE 11
ESTIMATED CHARACTERISTICS OF A 250 T/D H_2SO_4 PLANT
WITH 2.2-22 "SULFACID" TAIL GAS TREATMENT
UNDER VARYING ACID PLANT EFFICIENCIES

Acid Plant Conditions			Sulfacid Process Conditions				Supplementary Heat Requirements				Gas Saturation Requirements (3)	
Conversion Efficiency %	Tail Gas SO_2 Conc. ppm	Make-Up H_2O Requirements Lbs/Min	10% H_2SO_4 Recovered (As 100% H_2SO_4) Lbs/Min	Acid Conc. at Venturi Exit (1) %	Water Available for Make-Up Before Conc. in Venturi Lbs/Min	After Conc. in Venturi (2) Lbs/Min	Water to be Evaporated Lbs/Min	Heat Req'd Btu/Min	Nat. Gas SCFM	Recycle Acid Conc. %	Steam @ 50 psig Lbs/Min	Water Lbs/Min
99	833	41.6	3.24	24.4	29.2	10.1	0	0	0	10	113	15
98.5	1,250	41.6	4.87	16.4	43.8	24.7	0	0	0	16.4	113	15
98	1,670	41.6	6.49	14.1	58.4	39.3	0	0	0	14.1	113	15
97.5	2,080	41.6	8.12	13.1	73.1	54.0	12.4	16,200	16.2	16.3	98	13
97	2,500	41.6	9.73	12.5	87.6	68.5	26.9	35,800	35.8	19.0	79	11
96.5	2,920	41.6	11.35	12.0	102.2	83.1	41.5	58,000	58.0	21.4	59	8
96	3,330	41.6	13.0	11.7	117.0	97.9	56.3	81,000	81.0	23.8	37	5

BASIS: Acid Plant Product
Tail Gas Flow
Tail Gas Temperature
Ambient Air Humidity
Raw Material
 SO_2 Recovery Efficiency

98% H_2SO_4
18,700 CFM
154°F
.02 lb. H_2O /lb. Bone Dry Air
Sulfur
95%

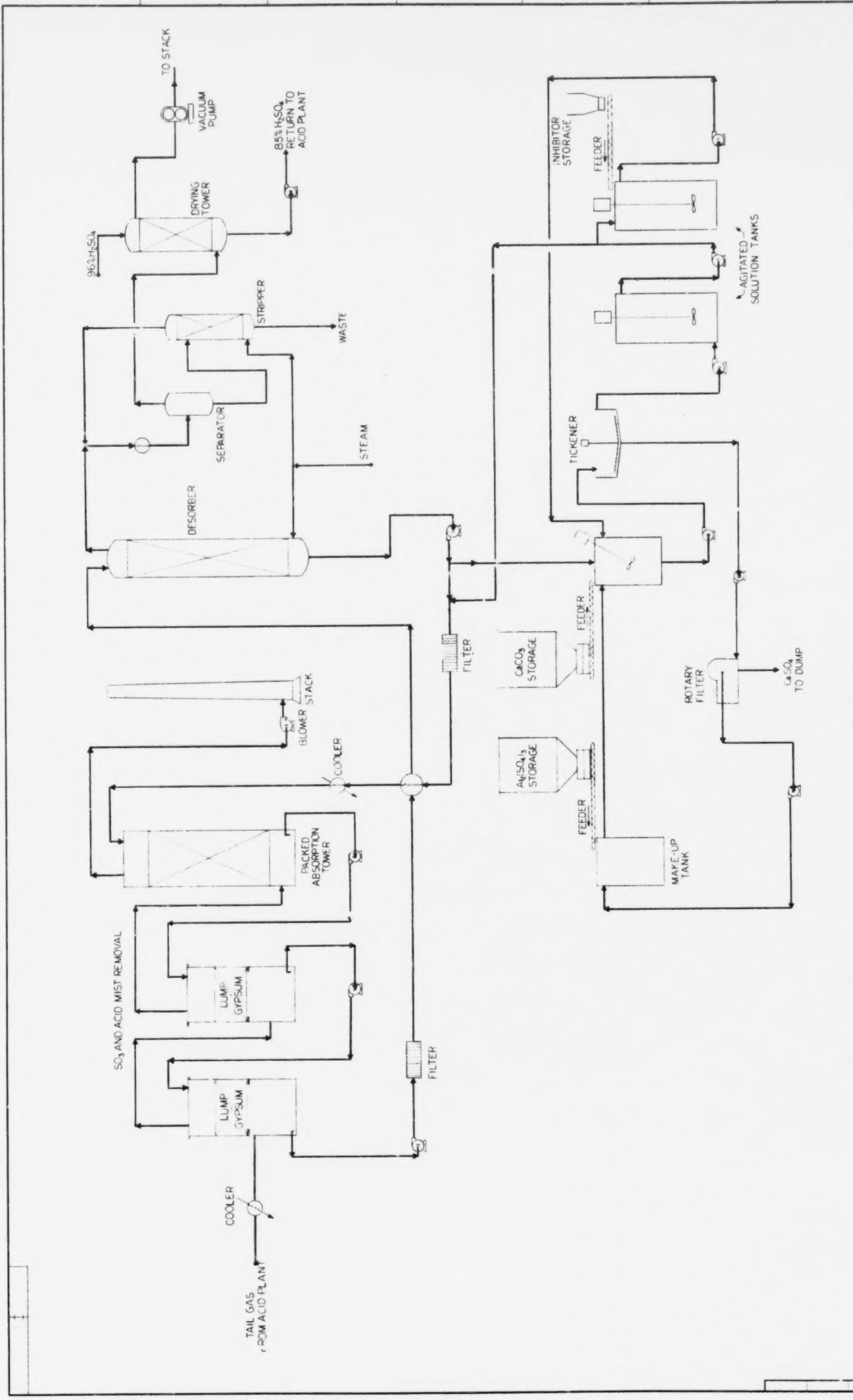
- (1) Based on Scrubbing with 10% Acid with no Supplementary Heat
- (2) With no Supplementary Heat
- (3) To Raise Inlet Temperature to Reactors to 125°F, Saturated

Absorption with Basic Aluminum Sulfate Solution, Regeneration with Heat to Release SO₂ (Hardman-Holden) (2.2.28)

This is an old chemical absorption process (Figure 22) in which basic aluminum sulfate solution reacts with SO₂ to form a complex compound. SO₃ vapor is also absorbed, but the mist is likely to pass through untouched, and should be removed before the gas is treated. The SO₂ is recovered by steam stripping the solution, condensing the excess steam, and recycling the wet SO₂ gas to the plant. The SO₃ pick-up, and build-up, in the absorbent solution is controlled by reacting a side stream of the stripped liquor with calcium carbonate. The sulfate is filtered off. The calcium content can be further reduced by adding some sulfite rich solution to the filtrate and polish filtering the product before recycling.

The major disadvantage of the process is the corrosive nature of the absorbent. A second potential problem is the precipitation of insoluble complex compounds in the packed towers. The solution is meta stable through certain of the operating temperature-composition ranges. Methods of preventing or minimizing the effects of these precipitates have not been demonstrated commercially.

The Hardman-Holden process is presently in operation in Europe, in connection with a sulfur dioxide producing plant. The process can be expected to achieve a control effectiveness of 200 ppm and possibly lower. The SO₂ content of the feed gas stream does not effect the sizing of the equipment. To achieve a greater control effectiveness the only change necessary is to increase the height of the packed section of the absorber. Steam consumption is lower than many other steam stripping processes.



REVISIONS		LIST OF SHEETS		TITLES		DATE		BY		CHECKED		DATE		BY		CHECKED	
NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION	NO.	DESCRIPTION
1	AS DESIGNED	1	TAIL GAS RECOVERY PROCESS 22.28	1	ALUMINUM SULFATE SOLUTION, REGENERATION WITH HEAT TO RELEASE SO ₂	1	(HARDMAN-HOLDEN)	1	0064C	1	FIG. 22	1	P	1		1	

The most troublesome of the tower fouling problems is the deposition of calcium sulfate in the inlet tower in the absorption train. This precipitate cannot be removed by chemical means. Present thinking leans to a pair of short gypsum packed guard towers which can be dumped every few months. The mechanisms for the precipitate formation are not understood.

The liming step for sulfate removal leaves the solution saturated with CaSO_4 . The incoming gases contain some SO_3 and also the SO_2 in solution reacts to form SO_3 with dissolved oxygen. The increase in the sulfate level precipitates the calcium though why it is confined to the first tower is not known. The SO_2 oxidation is catalysed by these compounds which are continuously removed by reaction with copper sulfate.

Similar sulfate removal problems must occur in other alkali absorption systems. Liming for sulfate removal may be expected to cause the same problems in the absorption towers. Ion exchange may be economic in other systems, but the basic aluminum sulfate system cannot tolerate more than traces of the monovalent alkalis.

The on stream factor for process 2.2.28 is likely to be lower than that of the acid plant due to fouling problems. The space requirements for this process are comparatively high, being in the order of 4,000-5,000 square feet for a 250 T/D H_2SO_4 plant. The systems will require the attention of a full time operator.

While this process has been in commercial operation for over 30 years, very little has been done to improve its operation. Development work would be required to find a suitable method for initial removal of SO_3 and acid mist and to reduce the fouling problems.

Resin Adsorption Process (2.2.29)

This process is illustrated by Figure 23.

The collector for the acid components of the gas stream is a polymer containing basic groups along its chain. The marco structure is such that diffusion into the core of the 20 mesh granule is very rapid and subsequent diffusion through the solid polymer of the matrix is sufficiently rapid to be economic in gas phase adsorption. The heats of adsorption depend on the acid component involved.

SO_2 can be desorbed by heating to about 220°F . The bonding with SO_3 is such that thermal desorption is impractical and chemical means must be employed.

The economics of the recovery of SO_2 from acid plant tail gases dictate the removal of the H_2SO_4 or SO_3 before the adsorption of SO_2 . A separate resin bed could be used for this purpose which bed would be periodically regenerated chemically. A more direct approach is the reaction of the SO_3 with a chemical such as lime or soda ash. The chemical reagent can, in theory, be in aqueous solution but sulfuric acid mist is expensive to remove by such media. The alternate is preheating the gas to evaporate all mist and passing it through a bed of highly porous lump lime or soda ash briquettes whereby gaseous SO_3 reacts with the solid.

In view of the very high ratio of SO_2 to SO_3 the adsorption media transforms first to the sulfite and then to the sulfate. The kinetics of this approach are under investigation.

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The SO_2 is adsorbed on the resin at about 100°F and stripped off at about $200\text{-}220^\circ\text{F}$. To simplify the stripping process a dried acid plant air stream is passed through the bed and returned to the acid plant.

Resin life has not been firmly established but appears to be about two years based on laboratory work. The life depends strongly on the regeneration temperature as might be expected for an organic compound. Its degradation rate is not a simple function of its residual capacity and the function itself may change with regeneration temperature suggesting a strong dependence on the exact local polymer structure.

The system has not been piloted. Laboratory development to date has been conducted by Rohm and Haas, who hold the patents for the resin.

The resin has an adsorption capability to achieve theoretically, a control effectiveness of near zero ppm SO_2 . The process is unaffected by the inlet SO_2 concentration, higher concentrations simply requiring more frequent resin regeneration. An actual control effectiveness well below 100 ppm is expected.

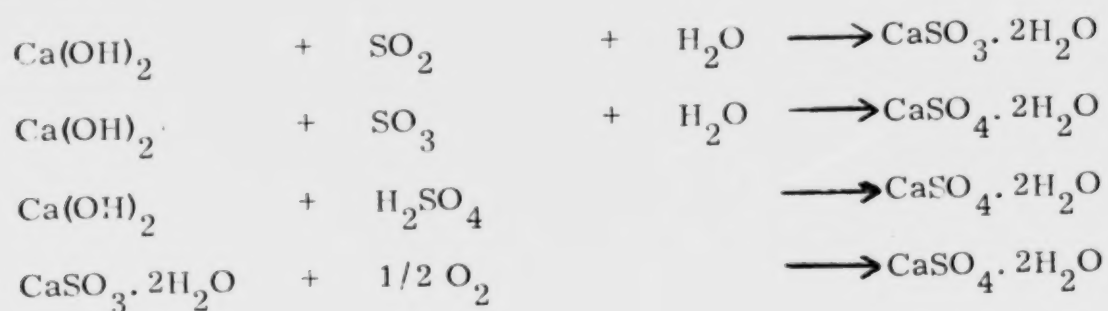
The process is simple and essentially automatic, requiring only part time operator attention. Space requirements for a unit to handle a 250 T/D acid plant are about 2,000 square feet.

Lime Absorption of SO₂ (2.3.3)

This is one of the simplest and most straight forward of the feasible processes. Variations of it are in commercial operation on utility power plants.

The objective of this process is to absorb the SO₂ in the tail gas with an inexpensive alkali and then dispose of the sulfur salt, as illustrated by Figure 24.

Sulfur dioxide, SO₃ and acid mist are absorbed in a single-stage venturi type scrubber. The scrubbing liquid is a slurry containing hydrated lime, calcium sulfite and sulfate. The reactions in the scrubber are as follows:

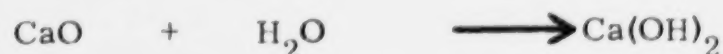


Following absorption the slurry is held in a delay tank to desaturate any calcium sulfate. This is done to avoid scaling out of this salt in the lines and the scrubber.

The bleed stream is drawn from the scrubber system to separate the sulfur salts equivalent to the sulfur gases being absorbed. Sulfite, sulfate and some alkali are settled out in the clarifier.

The underflow is centrifuged and the wet solids are sent to a storage hopper for disposal. The mother liquor is sent back to the scrubber

along with the overflow from the clarifier. Lime and make-up water are added to the scrubber system via a slaking tank:



An area in this process which may present processing problems is to achieve maximum utilization of the alkali which would be indicated by a very small percentage of free alkali in the waste solids.

Scaling of calcium sulfate must be investigated and proper delay times need to be established.

This process is simple, physically small and relatively inexpensive for a tail gas scrubbing process. The space requirements for a 250 T/D plant are only about 1,000 square feet. It may prove advantageous for small acid plants, for which the lime consumption and gypsum disposal would be minimal.

This process, unlike SO₂ recovery processes for tail gas clean up, does not give any incentive to push an acid plant to its maximum capability, since unreacted SO₂ is converted to a waste product rather than returned to the plant.

Process 2.3.3 requires only part time operator attention and should have a high on stream factor.

This process would be a useful back up to other scrubbing processes for use when a regeneration system is shut down. A stand-by storage tank for lime slurry might permit the acid plant to continue operation with good emission control until the regeneraor is back on line.

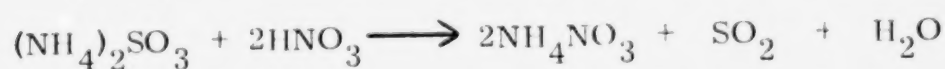
Ammonium Sulfite-Bisulfite Absorption with SO₂ Recovery and NH₄NO₃-Production (2.4.5)

This process, as illustrated by Figure 24, recovers most of the acid plant sulfur emissions as SO₂ for recycle to the plant and a small part as ammonium sulfate in an NH₄NO₃-(NH₄)₂SO₄ solution, containing about 16% N which might find a market locally as fertilizer. Sulfur dioxide is absorbed in two stages with ammonium sulfite-bisulfite solutions which are subsequently reacted with nitric acid to form ammonium nitrate and SO₂. The SO₂ is recycled to the acid plant and the ammonium nitrate is prepared for sale. Basically, this process is one of providing for the absorption of SO₂ from an acid plant tail gas as an intermediate step in the production of ammonium nitrate.

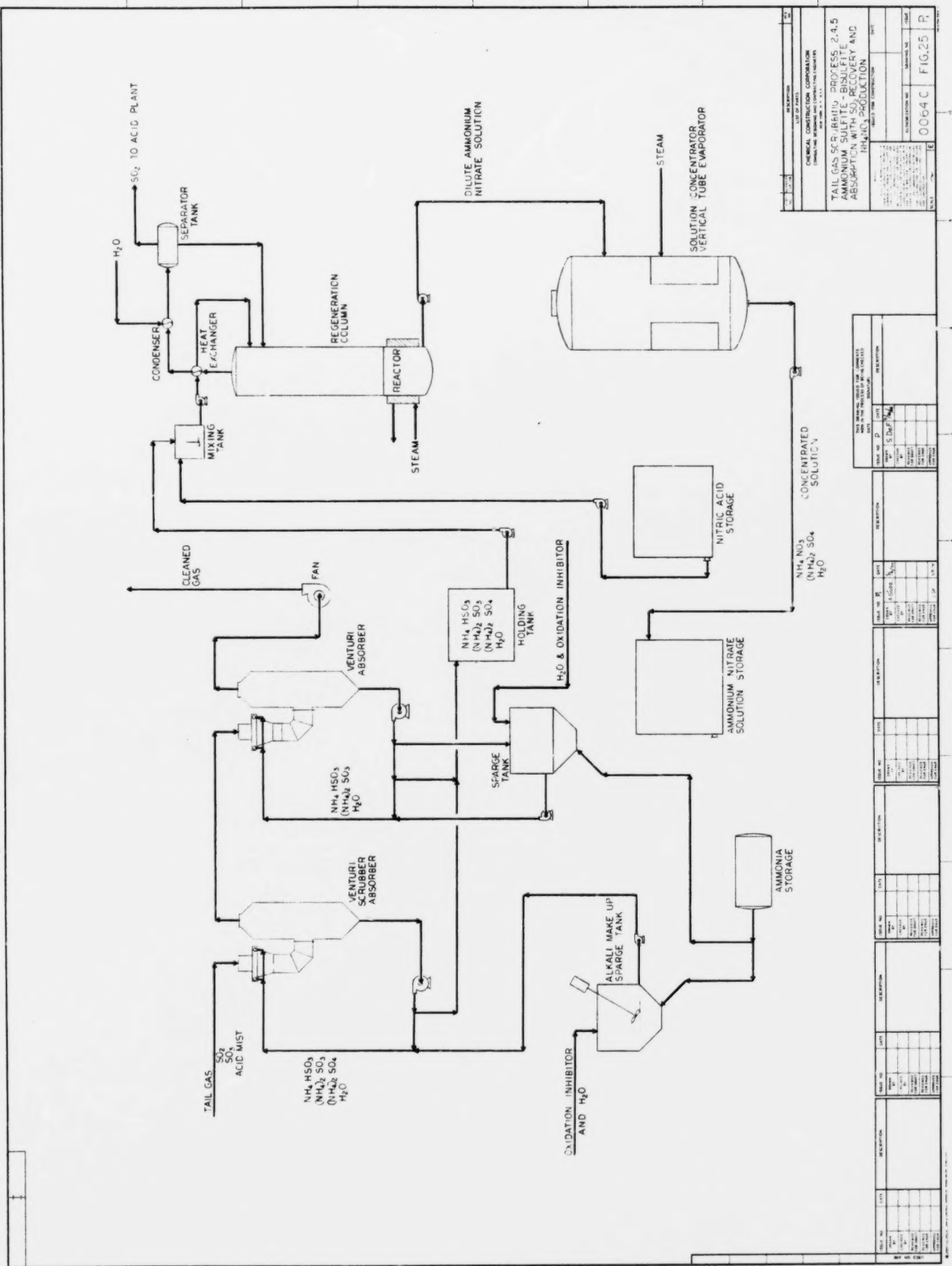
SO₂ is absorbed with the conversion of sulfite to bisulfite:-



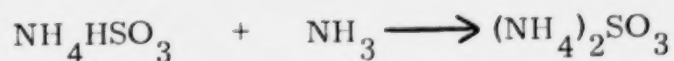
Amounts of bisulfite and sulfite equivalent to the SO₂ absorbed, minus the small amount of sulfite oxidized to sulfate, are bled from the absorption part of the system, mixed with nitric acid and passed into a steam heated reactor where the following reactions occur:-



The SO₂ recycle steam is indirectly cooled to about 110° F before it is returned to the acid plant. The ammonium nitrate solution containing a small amount of ammonium sulfate from acid mist and SO₃, as well as from sulfite oxidation, is concentrated in a vertical tube evaporator to a 45% NH₄NO₃ for sale.



Ammonia feedstock is added to both absorption stages to convert excess bisulfite to sulfite since one mole of SO_2 produces two moles of bisulfite.



Although this process is in operation in Europe, certain points require confirmation for complete evaluation. As with similar processes an oxidation inhibitor to minimize sulfate formation should be found.

The absorption stage should be piloted to confirm that the required SO_2 absorption can be achieved without significant loss of ammonia. The nitration reactor which is now being operated by the North Bohemian Chemical Works (SCHZ) at Lovosice, Czechoslovakia should be evaluated.

Since the by-product fertilizer solution is dilute and not a normal commercial grade, a market would have to be found within an economic distance from the plant. This will tend to restrict the number of potential applications of this system.

While this process is not particularly complex, the regeneration reactor column and vertical tube evaporator require careful attention and may tend to reduce the on stream factor somewhat; nevertheless, the process operates independently of the acid plant and will not affect its operation directly. Additional operator time equivalent to one man per shift should be allowed.

Space requirements for a plant sufficient for tail gas treatment for a 250 T/D acid plant is 2,000-3,000 square or more, depending upon NH_3 and product storage requirements.

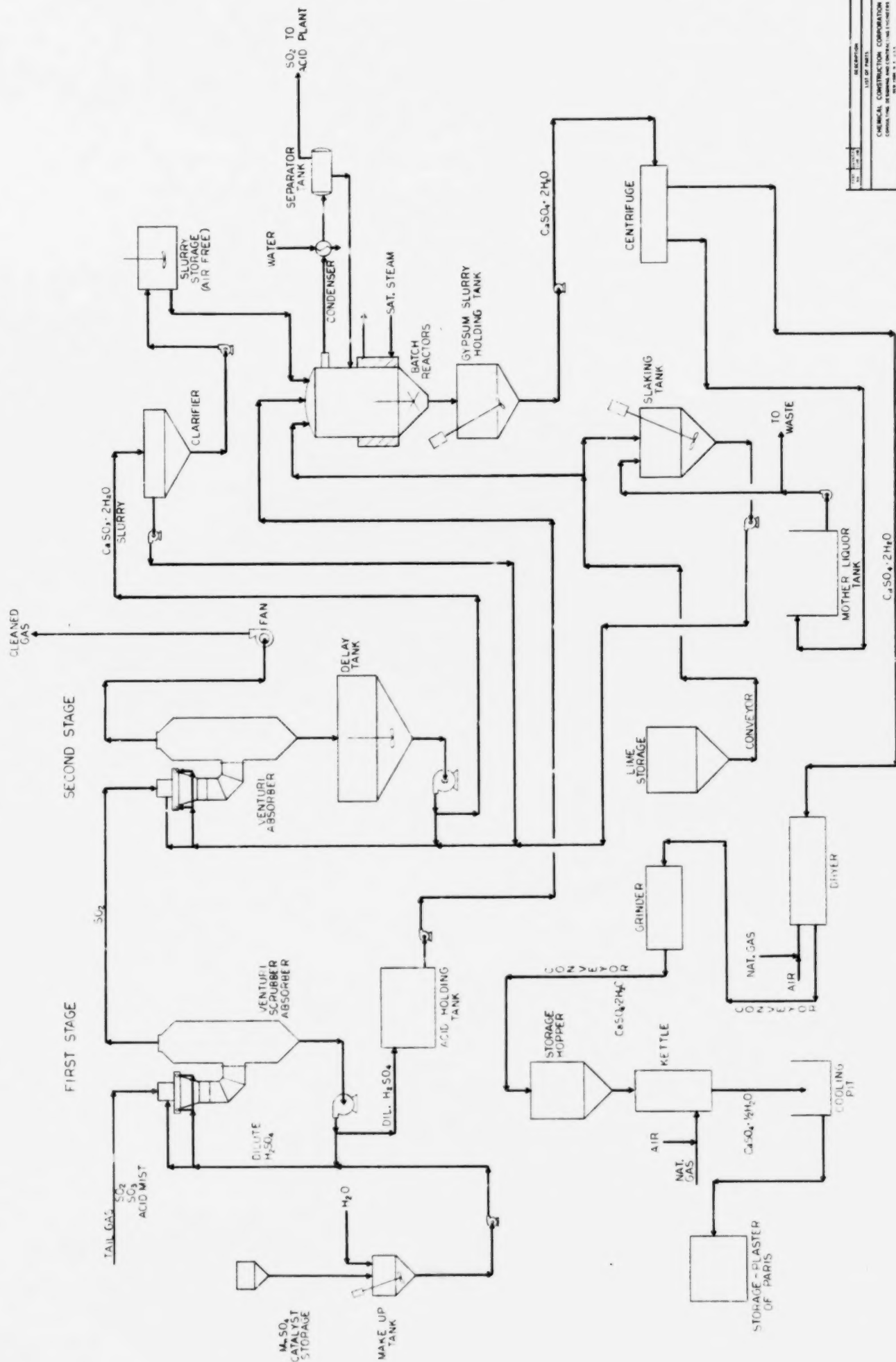
Sulfuric Acid-Lime 2-Stage Absorption to Recover SO_2 and Produce Plaster of Paris (2.4.6)

This process has neither been operated commercially nor piloted as a whole, though individual sections have been piloted. It is designed to achieve a control effectiveness of 100 ppm, removing SO_2 , SO_3 and acid mist to produce a salable plaster of paris ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and recycle a portion of the SO_2 to the H_2SO_4 plant.

About half of the SO_2 removed from the tail gas is oxidized to sulfuric acid in a first absorption stage and the remaining half is absorbed with lime in a second stage to form calcium sulfite. The sulfite is then reacted with the sulfuric acid from the first absorption stage to form calcium sulfate and SO_2 , the remaining half of which is recycled.

In the first stage the SO_2 is catalytically oxidized to sulfuric acid in the presence of a small amount of manganous sulfate. Acid mist and SO_2 are also removed at this point. The acid concentration is maintained at about 10% and this is reacted with the calcium sulfite slurry coming from the second absorption stage. An oxidation inhibitor may be added to the second stage to minimize sulfate formation. Any calcium sulfate formed here represents a loss of recycle SO_2 as well as an excess of dilute acid which must be disposed of.

Batch reactors are used for the conversion of calcium sulfite and sulfuric acid to gypsum and SO_2 . The evolved SO_2 is indirectly cooled to about 110°F before it is recycled to the acid plant. The gypsum slurry formed is centrifuged and then dried at about 260°F . The dried material is ground to a fineness of 70-80% through 100 mesh before being sent to a reactor where the gypsum is converted to



LIST OF SHEETS		REVISION	
NO.	DESCRIPTION	DATE	BY
1	TAIL GAS SCRUBBING PROCESS - 2, 4, 6		
2	SULFURIC ACID-LIME 2 STAGE ABSORPTION		
3	TO RECOVER SO ₂ AND PRODUCE		
4	PLASTER OF PARIS		
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plaster of paris:-



Natural gas is used as the fuel for the drying as well as for the conversion to the hemihydrate.

Several potential processing problems are apparent in this process. The catalytic oxidation of SO_2 in the first stage should be proven. A suitable oxidation inhibitor should be found for the second stage.

In addition to processing problems, a market for plaster of paris would be required to make this system economically attractive.

A batch reactor system which would require more than one additional man per shift plus a complex process makes this process less attractive than several others unless a market for $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ is available nearby. The control effectiveness is potentially high, but the on stream factor will probably be lower than the acid plant, although this will not affect the acid plant directly since the process operates independently.

D. FEASIBLE SYSTEMS FOR SO₃ AND ACID MIST CONTROL

Several processes which are feasible for SO₂ control will simultaneously provide control of acid mist and SO₃, either by choice or because the nature of the process requires that SO₃ and acid mist be removed prior to the removal of SO₂. Aside from these processes there are several processes and devices which are feasible for SO₃ and/or acid mist control, and which are suitable for application to sulfuric acid concentrators (process classifications 1.5 and 2.5) or to plants with dual absorption systems which do not themselves reduce the acid mist problem as the SO₂ emission level is reduced.

Many plants now operating incorporate pad type mist filters as described in 3.1.1 and which very economically reduce the level of acid mist emission as low as 2 mg/SCF, and remove essentially all particles > 3 microns. Removal of mist particles of < 3 microns is more costly, but not especially difficult, several feasible systems being available.

The feasible processes are listed in Table 12, which shows the removal efficiency for that portion of the mist above and below 3 micron particle sizes, and the emission level which may reasonably be expected for acid plants and for oleum plants, expressed in milligrams per standard cubic foot. The mist characteristics of these plants have been described in Part III. The aim in mist removal has been to eliminate a visible plume from the plant stack. Particles smaller than 3 microns will tend to form a visible plume at much lower quantitative emission

levels, thus the desirable control level varies with the characteristics of the mist at each plant. Mist forms from 10% to 30% of the total sulfur emission, and when uncontrolled it is often a real problem.

The various feasible methods included in Table 12 and described on subsequent pages, are:-

- 3. 1. 1 Dual Pad Mist Separators
- 3. 1. 2 Tubular Type Mist Separators
- 3. 1. 3 Panel Type Mist Separators
- 3. 2. 1 Electrostatic Precipitation
- 3. 3. 1 Mist Removal with Venturi Scrubber

The control of SO_3 can be accomplished with these devices only if moisture is added to first convert the SO_3 to H_2SO_4 mist. This occurs in a scrubber, such as process 3. 3. 1, but not with the other devices. Addition of moisture in these devices may introduce a serious corrosion problem, and seems to require time for the mist to form.

Introducing the exact stoichiometric water requirement is difficult because of variation in SO_3 content. A method of introduction to achieve proper distribution could also be a problem.

TABLE 12

FEASIBLE SYSTEMS FOR ACID MIST CONTROL

<u>Process</u>	<u>Efficiency ≥3 microns</u>	<u>Efficiency <3 microns</u>	<u>Emission Level 99% Acid Plants*</u>	<u>Emission Level Oleum Plants*</u>
3.1.1	99+%	15 - 30%	to 2 mg/SCF	to 5 mg/SCF
3.1.2	100 %	95 - 99+%	0.1 mg/SCF	0.1 mg/SCF
3.1.3	100 %	90 - 98%	0.5 mg/SCF	0.5 mg/SCF
3.2.1	99 %	Near 100%	0.5 mg/SCF	0.1 mg/SCF
3.3.1	98 %	Low	3 mg/SCF	Ineffective with <3 micron mist

* Based on manufacturer's generally expected results.

Dual Pad Mist Separator (3.1.1)

This is a simple, effective device in common use for removal of acid mist from absorption tower stacks. Generally, when operated at proper velocities, it will remove essentially all of the mist particles of 3 microns or larger.

Usually two pads are arranged horizontally in series in a section of reduced diameter atop the absorption tower, on top of which the stack is supported. Pads may be from 4 to 12 inches thick and are of knitted stainless steel wire or of teflon for H_2SO_4 service, supported on a stainless steel grid. The only operating cost is the power required to overcome the 2-3" W.G. pressure drop through the separator.

Entrained droplets and mist impinge on the mesh and are held momentarily, permitting larger drops to form which run off and fall back into the tower. Mist particles smaller than 3 microns, however, tend to pass through, only 15-30% being recovered. This type of unit is not as effective on plants with larger quantities of very fine mist such as occurs in an oleum plant.

Installation is relatively simple in existing plants as well as new plants, and requires no additional plant area, no additional operators and does not affect plant on stream factor.

Tubular Type Mist Separator (3.1.2)

This type of unit consists of multiple vertical tubular elements formed from packed glass fibre hung from a tubesheet located in the top of the acid plant absorption tower, or for an existing plant, often in a separate vessel which may be located on top of the absorption tower if conditions permit, or adjacent to the absorption tower at grade, or in the base of the stack.

This type of unit is very efficient, and since they are designed so that Brownian movement is the controlling mechanism for mist collection, smaller particles whose Brownian movement is greater, are collected with high efficiency, so that visible plumes may be eliminated even from oleum plants. The efficiency of this device is affected very little by gas velocity. Pressure drop through the mist separator element is on the order of 8" W.G.; however, the total pressure drop of the system depends upon the arrangement used.

When installed in an absorption tower, the tower height must be increased, or a separate vessel of similar construction provided to house the filter elements. The elements are of glass fibre, but ceramic elements have also been used. Droplets fall by gravity down the inside of the tube and are collected in a seal pot. The collected acid either falls or is pumped to the absorption tower depending upon the arrangement used. When an external vessel at grade is required, the cost of the system is substantially increased since a foundation, acid reservoir, acid pump, ductwork, and often a booster fan must be included.

Variation in packing materials and density can provide a variety of removal efficiencies in the < 3 micron range, but at very little differential cost.

Panel Type Mist Separators (3. 1. 3)

This type of unit consists of a many sided chamber situated in the top of an absorption tower or in a separate vessel. The vertical sides are provided with glass wool panels and the bottom is a steel plate sloped to drain collected acid toward the center of the chamber. Tail gas enters from the outside and as it passes through the elements droplets collect on the inner side of the panels, fall by gravity to the bottom and are returned to the absorption tower.

The unit is very efficient for most applications except for very strict control of oleum plants. Pressure drop through the elements is low, (6-8" W.G.) but total pressure drop depends upon arrangement.

For new installations the unit can be accommodated by extending the absorption tower height to include it. In this case, collected acid is returned directly through a drip leg. For existing plants, however, it is usually necessary to provide a separate vessel for the separator and to pump collected acid back to the absorption tower. A booster fan would probably be required, as well.

As with other mist control devices, this is very reliable, requires no attention and little maintenance.

Electrostatic Precipitation (3.2.1)

This type of equipment has been used for satisfactory mist control for many years in the purification section of wet gas plants, and was also used on drum concentrators for mist and spray control. These devices were lead lined with vertical tubes, lead being required because of the corrosive nature of dilute H_2SO_4 . Recently a variation of this equipment has been used successfully on tail gases from acid plants. For this service, the equipment is constructed of mild steel with long vertical panels dividing the precipitator shell into ducts which are charged to attract mist particles.

This equipment is most effective on the smallest mist particles, and can be provided with overall efficiencies up to 99%. Electrostatic precipitators should be very effective on oleum plants. Velocities must be low, 3-5 feet/sec., but pressure drop is usually less than 1" W.G., which means that no auxiliary blower is likely to be required. Efficiency is increased by increasing the length of duct, or residence time. Power requirements are nominal, ranging from 25 KVA for a 50 T/D acid plant to 90 KVA for 1,500 T/D.

One drawback is relatively large physical size of the equipment, ranging from 5' x 11' x 25' H for a 150 T/D plant to 30' x 30' x 40' H for a 1,500 T/D unit.

For drum concentrator applications lead lined electrostatic units have been supplanted by venturi scrubbers which are less costly, although they continue to be used in wet gas purification.

Venturi Scrubber (3. 3. 1)

This is the same general type of unit as is employed in many tail gas recovery systems, and depends upon intimate contact in a restricted throat between the tail gas and sprays of circulated liquid to mechanically remove the mist. This type of unit is flexible as to capacity and is quite effective with mist >3 microns. It is not likely to be effective, however, on very fine mist which tends to behave as a gas. Many of these units are in operation on concentrators where mist is generally 3 micron and larger. The scrubbing medium for concentrators is weak acid which is gradually bled to the concentrator as makeup.

This equipment is very reliable and requires no additional operator attention. It is not large, but in most cases separate installations at grade would be required, as the unit does not lend itself for installation on an absorption tower.

E. EMISSION CONTROL FOR CHAMBER PROCESS ACID PLANTS

As has been shown in Part III, chamber process acid plants are relatively few in number, relatively small in capacity and have an emission problem which is different from the contact process plants, requiring different control processes. Emissions from chamber plants can be as much of a problem as those from contact plants. Because the chamber process is gradually disappearing little effort has been expended on control of this dual emission problem of sulfur dioxide and nitrogen oxides. Processes applicable to contact plants are not suitable for removal of nitrogen oxides and, likewise, processes applicable to nitric acid plants for NO_x control are not best for SO₂ control. Mist loadings are similar to those for non-oleum contact plants, and the same types of mist control devices are applicable.

In the process survey, three processes have been received for control of this dual problem, none of which may be considered feasible at present. A cursory review of the control cost for process 4.1.3, when applied to a rather large capacity chamber plant, gave a control cost of over \$8 per short ton, far in excess of the control costs for contact plant control processes. (Control cost is defined in Part V.) Based upon this finding, it is considered very doubtful that a chamber acid plant, if faced with a choice of installing a control system or shutting down, could justify economically the installation of a control system.

Moreover, from Table 1, we can see that very few chamber acid plants are located within designated AQCRs. We have removed them from detailed consideration in this section.

F. COMPARISON OF SYSTEMS

As for any other process or device, technical considerations for selection of an acid plant emission control system will include:-

- . Technical capability to achieve the required control effectiveness - by actual demonstration preferably.
- . On-stream reliability.
- . Simplicity.
- . Flexibility to handle varying concentrations; also, to be modified if necessary to comply with more stringent regulations in the future.

Of Lesser Importance

- . Installation will not interfere with acid plant operation.
- . No unfamiliar operations are required.
- . No new disposal problems are introduced, either of waste material or salable by-products.
- . Small space requirements.

An ideal system, in addition to all of the above, would require minimum operating cost and be applicable to all types of acid plants. At present, no such system has been developed.

It should be emphasized that the criteria for selection of a control system for application to a sulfuric acid plant are not necessarily the same as for other applications where gas flows,

compositions and temperatures are different and whose general operation are of a different nature, such as power plants and the like.

The systems described in this report fall into three general groups, the general capabilities of which are described and compared below.

In Plant Modifications for SO₂ Control

All dual absorption systems control SO₂ emissions only, and provide no control in themselves for SO₃ and acid mist. Their application is more limited than tail gas recovery systems, principally being applicable to sulfur burning plants. Their control effectiveness is expected to be better than 500 ppm. Application of dual absorption to an existing plant will require a careful study of space, accessibility for construction, and other factors of arrangement and design. Each installation will require individual, detailed engineering. They cannot be further modified to achieve a greater control effectiveness.

Dual absorption systems, on the other hand, present several distinct advantages to existing plants which can use them. The technology is conventional sulfuric acid technology which is presently offered with guarantees, commercially. Their on stream reliability is identical to that of the plant to which they may be applied. Flexibility of the acid plant itself will be increased, since the plant may be pushed to its maximum capability and still maintain a control effectiveness of 500 ppm. This is especially true for older, less efficient plants with large design safety factors, which might take excellent advantage of this possibility.

A new plant, designed for dual absorption from the start, will, additionally, through process design modifications, be able to take advantage of reduced sizes of major equipment. Such a plant will be simpler and less costly than an existing plant with an add-on system. With a new plant the arrangement problem of the add-on system is avoided.

The methods described in 1.3.4 for improved conversion meet all of the criteria technically required for the ideal system except one -- they cannot achieve a control effectiveness in the range being considered as a permissible emission level. It is possible that a reduction in plant capacity using these criteria to achieve, say 1,500 ppm, may result in a greater production cost per ton of acid than to build an "add-on" dual absorption system and run a plant at 25% above design capacity with a control effectiveness of 500 ppm.

Older plants, plants with multiple units, and wet gas plants tend to be more congested or hemmed in by other facilities, and probably would have difficulty in finding space within battery limits for in-plant control systems. An installation which would require extensive modification to existing facilities would require prolonged shutdown and would be prohibitively expensive.

Tail Gas Recovery Systems

Most tail gas recovery processes provide simultaneous control of SO_2 , SO_3 and acid mist to levels well below 500 ppm under ordinary plant operating conditions. The tail gas recovery processes are generally applicable, from the technical standpoint, to all classes of contact acid plants. Their greatest drawback technically at present is that most are not completely developed.

While tail gas recovery processes may or may not have the on-stream reliability of the H_2SO_4 plant with which they may be associated, this is not critical since such processes are not an integral part of the acid production process. If they are not operating the acid plant may continue to operate, but tail gas emissions will return to the condition existing before the control system was installed. Whether or not this is acceptable will depend upon local regulations. They also will have the considerable advantage of providing good control during the awkward periods when an acid plant is starting up or shutting down.

Generally, such systems are flexible with respect to the concentration of sulfur compounds in the tail gas which they can handle, although with high concentrations the SO_2 emissions may increase slightly they are still expected to be within presently proposed limits under almost all conditions.

In most cases, tail gas recovery processes are more complex than any type of in-plant process modification and will require additional personnel to operate. In this regard, those processes which produce by-products of any kind are the least desirable if other considerations are equal. The exception, of course, would be a plant in a unique situation where a convenient market at a good price existed for a given by-product.

Where an acid plant consists of several units together, all of which will require control systems, tail gas recovery systems may be very attractive economically. This is discussed in more detail in Part V.

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Tail gas recovery processes do not need to be integrated into the sulfuric acid plant battery limits, although it is desirable that they be located nearby. Only the SO_2 removal scrubbing portion of a process need be adjacent to the acid plant absorption tower. From an operational and mechanical standpoint it would not be desirable to locate the scrubbing section on top of the acid plant absorption tower.

Tail gas recovery systems will not need the careful individual design that add-on dual absorption requires; they can be fairly standardized package systems. For a group of units in one plant it would be logical and advantageous to install a scrubber on each unit with one centralized recovery system. Generally, tail gas recovery systems will require a larger area than the in-plant conversion systems.

By-product producing processes, aside from economic considerations, appear less desirable than those which recover SO_2 or acid for recycle to the acid plant. By-products which have been considered in the "feasible" processes are sodium sulfite, plaster of paris and ammonium nitrate/sulfate solution. The location of markets, assuming they can be found for these products, immediately limits the number of potential applications for the process. In order to realize some recovery of operating costs the producer must maintain some quality control, be able to meet delivery commitments and provide the necessary additional staff to perform these functions in addition to the actual handling of the material.

The nitrate (or sulfate) solution produced in process 2.4.5 (or 2.4.4) is more dilute than conventional commercial solution fertilizers, which immediately makes it less desirable, since twice the volume

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must be handled to achieve the same result as with commercial products. Additionally, this is a highly competitive market dominated by large producers.

Plaster of paris produced by process 2.4.6 will have a very restricted market, probably the best potential being for gypsum wall board producers. Another problem here will be the quantity of marketable by-product. A wall board manufacturer is not likely to be interested in a separate supply of a small fraction of his requirements.

Sodium sulfite, which was discussed with process 2.1.1, may have a better marketability, but does not generally appear as attractive as SO_2 recovery.

Producing a waste product such as calcium sulfite-sulfate in process 2.3.3, although a nuisance is not likely to be difficult to dispose of in the relatively small quantities under consideration.

In tail gas scrubbing processes water is evaporated and the gases are cooled during absorption of SO_2 . With processes using water slurries or dilute salt solutions for absorption the gases become saturated. The gases do not fully saturate, however, in processes employing concentrated salt solutions. Cooling gases increase their density, reducing effective stack height. The result is ground level SO_2 concentrations which are now as low as they would be if the tail gas was hot, but still much lower than the concentration without a control system. Saturation and near saturation of the gases causes condensation and produces a visible plume.

It appears that it may be desirable to reheat tail gases in some instances to reduce this problem. Several methods are available, such as direct heating or indirect heating to reduce density and increase velocity. Heat may be obtained from various sources including waste steam or calciner tail gas.

In summary, the tail gas recovery systems which best appear to meet the previously stated guidelines are, for each point:-

- . Technical Capability - Process 2.2.29 apparently has the best potential for control effectiveness.
- . Most Advanced in Development - Are probably 2.3.3, 2.2.6, 2.2.8, 2.2.22 and 2.2.28, although 2.2.22 is limited in potential applications.
- . Simplicity - Process 2.3.3.
- . Flexibility - Process 2.2.29 can achieve a control effectiveness of near zero regardless of inlet SO₂ concentrations.
- . No Unfamiliar Operations - Processes 2.3.3, 2.2.22, 2.2.29, 2.2.14 are best in this regard, although none of the "feasible processes" present very serious problems.
- . No Disposal Problems - Processes 2.2.6, 2.2.8, 2.2.14, 2.2.22, 2.2.28, 2.2.29 produce no waste or by-products. Process 2.2.22 (Sulfacid) meets this condition only if all dilute acid can be utilized within the plant.
- . Small Space Requirements - Process 2.3.3.

Mist Control Systems

Mist control systems, like dual absorption processes, control only a part of the total emission problem of contact acid plants. They can be applied to any type of acid plant, and a majority of operating plants today include some type of mist control device.

The effectiveness of various devices is governed to a large extent by the particle size distribution of the mist in the tail gas stream as well as the total quantity of mist. The on-stream factor for the feasible systems is as high or higher than the acid plant to which they might be applied.

All of the feasible devices reported are in commercial application on acid plants, as well as other types of plants.

To achieve an invisible plume from most plants, 3.1.2, 3.1.3 and 3.2.1 can achieve the necessary control effectiveness. To achieve a level of 3.0 mg/SCF all of the feasible systems could be effective on non-oleum plants. For oleum plants, however, 3.1.1 (dual mist pads) or 3.3.1 (venturi scrubber) would not provide effective control, since much of the mist is below 2 microns. Actual stack heights on existing plants vary from about 60 feet to 300 or more feet above ground-level.

Tail gas treating systems which remove acid mist with or prior to SO_2 removal would in all likelihood require no further mist control, but dual absorption processes will require mist control devices in addition to dual absorption equipment. The type to be added, if any, would be governed by the type of acid plant, as stated above.

V

ECONOMICS OF CONTROL

Preceding sections of this report have dealt with the technical capabilities and number of applications of various selected processes for control of emissions from sulfuric acid plants. It is apparent that there are several possible solutions to each problem which will achieve the same effectiveness of control. Most control processes have wide capabilities in the number and types of plants to which they may be applied. The third factor which must be considered is the economics of various control systems. To compare the various systems a comparison is made of "control cost", which may be defined as the incremental cost of H_2SO_4 production contributed by a control system. Control cost is determined by calculating the cost of producing one ton of acid in a plant with a given control system, and subtracting the cost of producing one ton of acid in the same plant without the control system, all on an annual basis, and taking into account the increased production of the more efficient plant with the control system. The cost of acid production in conventional plants of various types is shown in Figure 12, Part III.

The cost of production in a new 2.2 or 2.4 class plant may be considered the same as the production cost in modern 1.2 or 1.4 plant for purposes of this study.

A. SELECTION OF UNIT COSTS

The various control systems utilize various chemicals which are not normally used in acid plants. The unit costs used for these various chemicals in calculating control costs are listed below:-

Ammonia	\$ 50/short ton
MnSO ₄	\$100/short ton
Lime (CaO)	\$ 15-16/short ton
Plaster of Paris (CaSO ₄ · 1/2H ₂ O)	\$ 10/short ton
Fuel Oil #6	\$.07/gallon
MgO	\$ 50/short ton
K ₂ CO ₃	\$.11/lb.
Oxidation Inhibitor	\$1.25/lb.
Ammonium Nitrate- Ammonium Sulfate Solution (16.7% N)	\$22.50/short ton
100% HNO ₃ (as 57%)	\$ 80/short ton
Na ₂ SO ₃	\$ 35/short ton
Na ₂ CO ₃	\$ 33/short ton
Natural Gas	\$.30/MBTU
Waste Disposal	\$ 2/short ton of disposable material
Methylamine	\$.20/lb.
Alumina	\$ 60/ton

B. SELECTION OF OTHER OPERATING COST FACTORS

For dual absorption systems of any type it is not likely that additional operators would be required, since the equipment operates in the same manner as the other equipment in the plant, and requires no more attention. Add-on systems which are separate processes will probably require some additional operator attention. Systems with mechanical solids handling equipment and batch type operations require an additional full time operator. When a by-product of some type must be handled an additional part-time operator may be required. Simple processes and all gas-liquid systems will probably require only part time attention by another operator. This was discussed in more detail for each of the processes described as feasible.

Maintenance costs for mechanical solids handling equipment generally exceed the 4% figure used, but in these plants the equipment represents a small part of the whole plant and generally is operated at a fraction of its rated capacity, therefore, we have held to 4% overall.

Overhead is taken as 70% of the sum of operating labor, supervision and maintenance. This is approximately equal to 100% of operating labor, supervision and the labor portion of maintenance, and has been used as a convenience in calculating control costs.

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Interest, depreciation, taxes and insurance are charged at the same rates used for the base plants. When applied to plants of classifications 1.1 and 1.3, interest and depreciation is included for the control system cost only, since the plant is assumed to be over 10 years old, and fully amortized.

C. CAPITAL INVESTMENT REQUIREMENTS

Since charges related to capital investment form a part of acid production cost, including the cost of emission control, it was necessary to prepare approximate cost estimates for each of the processes described in Part IV. As the number of possible combinations is practically unlimited, several examples were selected for a variety of plant capacities and emission levels. Costs for several systems were estimated for the same sets of conditions so that results would be comparable. Recognizing that other factors such as inlet concentration, control effectiveness and plant capacity affect different processes in different ways, cost estimates of selected processes were made under different sets of conditions to permit the calculation of control costs with respect to these other variables.

As the basic reference point a nominal plant capacity, (which here means plant capacity at normal operating conditions before inclusion of a control system) was selected at 250 ST/D. Most processes were costed to fit three different classes of acid plants, 1.1, 1.2 and 1.4, as applicable, under the following flow rates and emission levels:-

<u>Class</u>	<u>Emission Level</u>	<u>Tail Gas Flow Rate</u>
1.1	5,000 ppm	18,700 ACFM
1.2	2,500 ppm	18,700 ACFM
1.2	4,000 ppm	18,700 ACFM
1.4	3,200 ppm	29,200 ACFM

Very little was done with applications class 1.3 plants, as it is expected that the relationship in control costs between 1.3 and 1.4 plants will be similar to that between 1.1 and 1.2 for a given control system.

For the design of the recovery process the tail gas was assumed to be discharged at 154⁰F in all cases. Estimates are for approximate U.S. erected costs under typical current conditions, exclusive of any site clearing, land costs or royalties. Selected processes were also estimated for nominal acid plant capacities of 50, 750 and 1,500 ST/D.

Tabulations of these estimated capital costs are presented in Tables 13, 14 and 15. Similar information is presented graphically in Figure 27. Process 2.2.22 is not included in the tabulation, since accurate information was not available to permit estimating under the selected base conditions. The only cost data⁽¹⁾ available for 2.2.22 applied to an acid plant is for a 396 T/D acid plant emitting 1,800 ppm SO₂. This cost was modified to add a quencher and convert to current U.S. basis. Control costs for this process are calculated for this condition only, and are not comparable to other control costs. 1,800 ppm is not a realistic emission level in the U.S., and the cost variation of this process with SO₂ concentration was not available to us.

Variations in Capital Investment Requirements

Various factors which affect investment requirements, other than capacity, were mentioned previously. The effect of these factors is not always the same for all types of processes, as shown by the following examples.

- (1) Ellwood, Peter - "Versatility Is the Word For SO₂-Removal Process" -Chemical Engineering, June 16, 1969

Variation With Acid Plant Capacity

With inplant modifications such as dual absorption, the cost of added equipment all varies with plant capacity, since its sizing is basically determined by gas flow through the plant. Tail gas recovery systems, on the other hand, actually consist of two sections - a sulfur removal scrubbing operation whose size and cost is basically determined by the tail gas flow, and a recovery section whose size and cost is governed only by the quantity of sulfur values recovered. For example, a class 1.1 250 T/D sulfur burning plant, with a stack containing 5,000 ppm SO_2 in 18,700 ACFM will require the same recovery section as a 500 T/D plant with a stack containing 2,500 ppm SO_2 in 37,400 ACFM of tail gas. The scrubbing sections, however, will vary by a capacity factor of two. This is true regardless of the absorption process used. In some processes the absorption section is large and the recovery section is small; in others the opposite may be true. This is a cost factor which must be taken into consideration when selecting a system for a specific situation.

From Figure 27 it may be seen that capital cost of control systems for the same emission level vary widely with acid plant capacity. Process 2.2.29, for example, is low for small plants, high for large plants due to the direct variation of resin requirements with acid plant capacity. Process 2.2.6, on the other hand, is high for small plants but relatively less expensive for large plants, for reasons discussed in preceeding paragraphs.

Variation With Control System Capability

Some tail gas recovery processes, notably 2.1.1 and 2.2.6, may be operated to recover SO_2 only, or to remove SO_2 plus SO_3 and acid mist.

Process 2.2.6, for example, will recover acid mist and SO_3 along with SO_2 by a variation in scrubber design and an increase in the fan horsepower to overcome the additional pressure drop. The difference in capital investment is slight, and the SO_3 -mist problem is reduced, at an additional cost of perhaps \$20,000 for a 250 T/D plant, which is less than 5% of the 2.2.6 control system cost.

Variation in Inlet Conditions to Tail Gas Recovery Systems

For tail gas recovery processes we have seen that the size and cost of the recovery section of the process varies with the SO_2 content of the tail gas. Since the quantities of material being handled in the recovery section of a tail gas recovery process are very small by chemical plant standards, the actual capacity of equipment very often may be greater than required capacity simply because no smaller commercial continuous service equipment is available. This is especially true for solids handling equipment which is generally flexible in its capability to handle variations in capacity. Since the tail gas scrubbing section is not affected at all by inlet SO_2 concentration, the overall result is that most processes vary only slightly in cost due to variations in inlet concentration. The advantages resulting from this will be discussed under Control Cost.

For mist control systems the cost for any one type varies with flow rate of the tail gas. With proper velocities most control devices will achieve the same effectiveness, regardless of mist loading.

Variation With Control Effectiveness

In-plant modifications to achieve dual absorption will normally result in a control effectiveness of 500 ppm SO_2 . Equipment size and cost

depends on plant capacity rather than on control effectiveness, and there would be little if any, cost reduction if a lower figure was chosen.

Tail gas treatment systems can vary in effectiveness by varying the circulation in the absorption system. The only effects on capital cost would be on the circulator pump size and the recovery section, which would be changed only slightly. For example, to control from 4,000 to 500 ppm rather than 4,000 to 200 ppm would result in less than 10% reduction in the capacity of the recovery portion of a tail gas control system. Absorbant composition can also change effectiveness.

Variation Between Costs for Existing and New Plants

Generally application of a control system to a new plant will be less costly than applying the same system to an existing plant, as well as producing a more desirable plant arrangement, since the plot plan will have provided for the control system at the outset.

Tail gas recovery systems, if included in the original design, may eliminate the need for mist control devices on the absorption tower as well as the need for a very high stack. It may be possible to eliminate a separate fan in the absorption section of the control process.

When designing new plants using tail gas control systems which return SO_2 to the acid plant it may be possible to effect savings by reducing efficiency in the contact plant itself, as the sulfur losses are recovered in the control system.

Mist control devices can be accommodated more economically on new plants than old, principally because in new plants the devices may be

incorporated into the absorption tower, while for existing plants an external installation is often required.

Capital Cost Savings for Multiple Units with One Control System

Tail gas recovery processes, which consist of a removal section and a recovery section, can be applied to multiple acid plant units at one location at a significant saving over installation of individual systems on each unit of the acid plant. For this situation, a separate removal scrubbing or absorption unit would be installed on each acid production unit. The bleed streams for recovery would be treated in a single recovery section. Significant savings would be realized in the capital cost of the recovery unit, as well as reduction of design engineering costs.

APPROXIMATE CAPITAL INVESTMENT REQUIREMENTS

SO₂ CONTROL SYSTEMS APPLIED TO 250 T/D H₂SO₄ PLANTS[illegible]

TABLE 14

ESTIMATED CAPITAL INVESTMENT REQUIREMENTSFORSELECTED SO₂ EMISSION CONTROL PROCESSESATVARIOUS PLANT CAPACITIES

<u>Process</u>	<u>Initial Emission Level</u>	<u>Control Effectiveness ppm</u>	<u>50 ST/D</u>	<u>250 ST/D</u>	<u>750 ST/D</u>	<u>1500 ST/D</u>
1.1.1 Dual Absorption (new plant, sulfur burning)	---	500	\$	\$1,300,000	\$2,500,000	\$3,700,000
1.2.2/1.2 Add-On Dual Absorption	4,000	500	260,000	482,000	920,000	1,450,000
2.2.6/1.2 MgO Absorption	4,000	200	285,000	510,000	780,000	1,045,000
2.2.14/1.2 Methylamine SO ₃ -HSO ₃ Abs.	4,000	200	270,000	465,000	765,000	1,080,000
2.2.29/1.2 Resin Absorption	4,000	-0-	195,000	442,000	870,000	1,312,000
2.3.3/1.2 Lime Absorption	4,000	200	180,000	285,000	425,000	570,000

TABLE 15
APPROXIMATE CAPITAL INVESTMENT REQUIREMENTS
FOR VARIOUS
ACID MIST CONTROL SYSTEMS

Control System	New Plants				Existing Plants			
	50 T/D 3,750 ACFM	250 T/D 18,700 ACFM	750 T/D 56,000 ACFM	1,500 T/D 112,000 ACFM	50 T/D 3,750 ACFM	250 T/D 18,700 ACFM	750 T/D 56,000 ACFM	1,500 T/D 112,000 ACFM
3.1.1 Dual Mesh Pads	\$ 10,000	\$ 20,000	\$ 28,000	\$ 38,000	\$ 13,000	\$ 25,000	\$ 35,000	\$ 48,000
3.1.2 Tubular Fibre Type	55,000	70,000	105,000	170,000	78,000	100,000	150,000	240,000
3.1.3 Panel Fibre Type	14,000	23,000	55,000	95,000	27,000	44,000	105,000	170,000
3.2.1 Electrostatic	60,000	85,000	105,000	200,000	60,000	85,000	105,000	200,000
3.3.1 Venturi Scrubber		70,000				70,000		

NOTE:

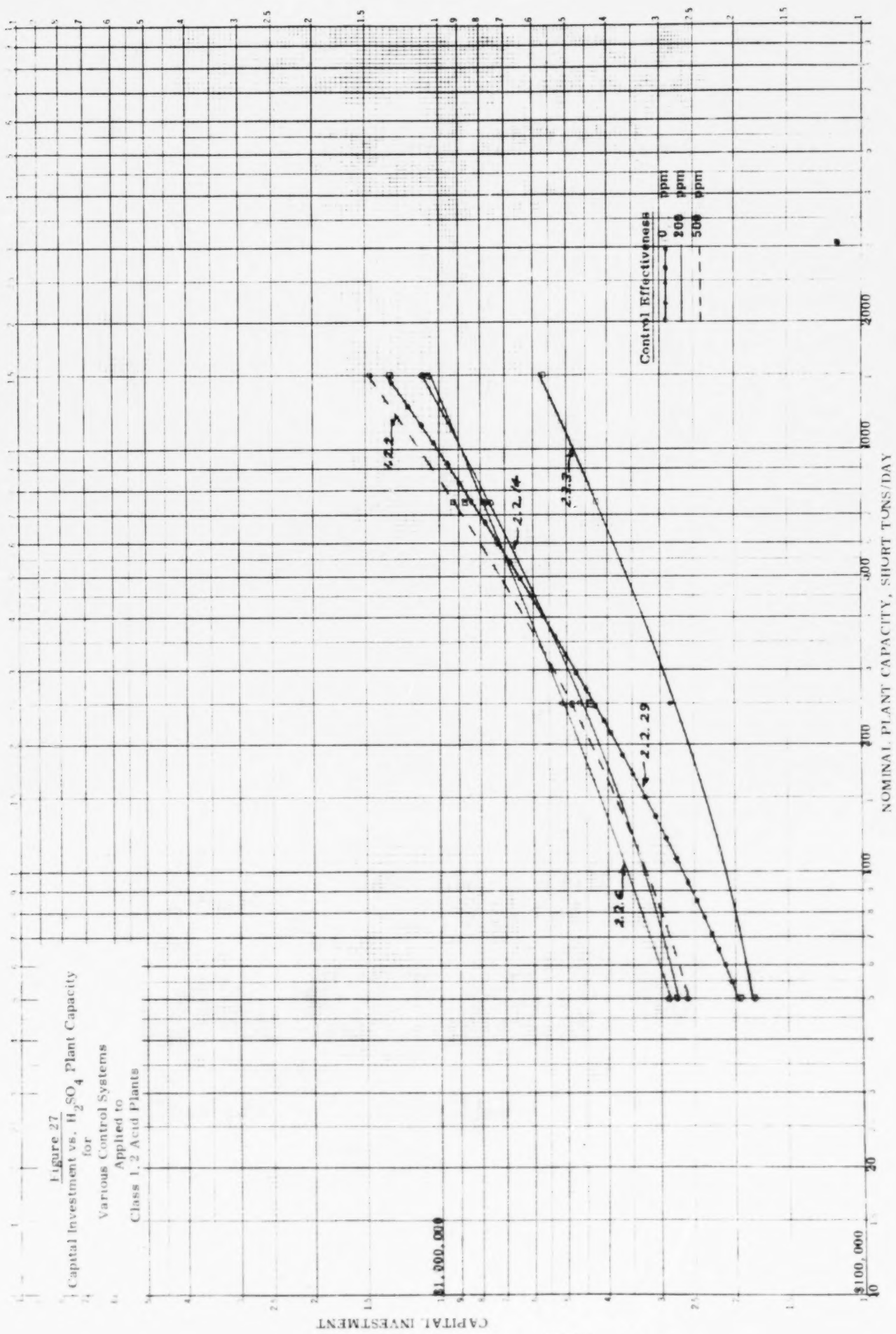
Size and cost depends upon tail gas flow rate.

Costs are given for class 1.2 sulfur burning plants.

Adjustments proportional to gas flow must be made for various wet gas plants.

See Part III.

Figure 27
Capital Investment vs. H_2SO_4 Plant Capacity
for
Various Control Systems
Applied to
Class 1, 2 Acid Plants



D. CONTROL COST

Control cost, as used in this report, may be defined as the incremental production cost per ton of acid produced caused by application of a control system to a plant or unit to achieve a selected control effectiveness. As discussed previously, it may be possible to achieve various levels of control effectiveness with a selected process, and thus have different control costs for the same system.

Control costs calculated for various "feasible" processes as applied to different classes of plants and at different control effectiveness levels are given in Table 16. Details of the control costs are shown in the appendix.

In the calculation of control cost the following basic assumptions have been made. Where additional acid is produced it is assumed that this is desirable and that it can be marketed at the same prevailing price as all other acid. Where a by-product is made, the cost of selling of the by-product has not been accounted for, but must be deducted from the selling price.

Control cost is calculated by determining the cost per ton of acid produced on an annual basis from a class of plant with a control system, then deducting the cost per ton of acid produced on an annual basis by the basic plant from it.

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The control costs for mist control only are small for most systems, as can be seen from Table 16(c). The principal cause for variation in control cost in using these devices is not control effectiveness, inlet concentration or type of plant, but whether the plant is new or existing. For most systems there is a marked saving when the system is provided initially over the cost of adding one later. The exceptions are 3.2.1 and 3.3.1 which are normally external units not incorporated with the absorption tower in any case.

For other types of processes the causes for variation in control costs are discussed in the subsequent paragraphs.

TABLE 16a
CONTROL COSTS FOR VARIOUS DUAL ABSORPTION PROCESSES
APPLIED TO
VARIOUS TYPES, CAPACITIES AND EFFICIENCIES OF ACID PLANTS
FOR
500 PPM SO₂ CONTROL EFFECTIVENESS

Process	Initial Emission Level	Without Supplementary Production			With Supplementary Production (2)		
		50 T/D	250 T/D	1,500 T/D	50 T/D	250 T/D	1,500 T/D
1.1.1 Dual Absorption (1)	---	\$	\$.41	\$.18	\$	\$	\$
1.2.1/1.1	5,000		1.44				
1.2.1/1.2	4,000		1.48				
1.2.2/1.1	5,000	3.50	1.36	.78	2.30	.92	.59
1.2.2/1.2	4,000		1.39	.95		.73	.51
1.2.3/1.4	3,200		2.31				.48

(1) Compared to class 1.2 acid plant

(2) About 15%

TABLE 16b
CONTROL COST FOR VARIOUS TAIL GAS RECOVERY PROCESSES
APPLIED TO
VARIOUS TYPES, CAPACITIES AND EFFICIENCIES OF ACID PLANTS
FOR SO₂, SO₃ AND MIST CONTROL

Process	Emission Level		50 T/D	250 T/D	750 T/D	1,500 T/D
	In	Out				
2.1.1/1.1	5,000 ppm	250 ppm	\$	\$ 3.13	\$	\$
2.1.1/1.2	4,000	200		3.05		
2.2.6/1.1*	5,000	250		2.57		
2.2.6/1.2*	4,000	200	8.61	2.37	1.05	.68
2.2.6/1.2*	2,500	125		2.36		
2.2.6/1.2*	2,000	100		2.35		
2.2.6/1.4*	3,200	160		2.70		
2.2.6/1.1	5,000	250		2.71		
2.2.6/1.2	4,000	200	8.82	2.51	1.18	.80
2.2.6/1.2	2,500	125	8.70	2.51	1.15	.78
2.2.6/1.4	3,200	160		2.92		
2.2.8/1.1	5,000	250		2.84		
2.2.8/1.2	4,000	200		2.73		
2.2.8/1.4	3,200	160		2.35		
2.2.14/1.1	5,000	250		1.98		
2.2.14/1.2	4,000	200	6.10	1.88	1.03	.78
2.2.14/1.4	3,200	160		2.58		
2.2.28/1.1	5,000	500		2.87		
2.2.28/1.1	5,000	250		2.87		
2.2.28/1.2	4,000	200		2.96		
2.2.29/1.1	5,000	-0-		1.50		
2.2.29/1.2	4,000	-0-	4.15	1.63	1.08	.86
2.3.3/1.1	5,000	250		2.33		
2.3.3/1.2	4,000	200	6.00	2.14	1.33	.94
2.3.3/1.4	3,200	160		2.48		
2.4.5/1.1	5,000	250		2.63		
2.4.5/1.2	4,000	200		2.52		
2.4.5/1.4	3,200	160		3.05		
2.4.6/1.1	5,000	250		3.50		
2.4.6/1.2	4,000	200		3.33		
2.4.6/1.4	3,200	160		3.76		

* SO₂ Emission Control Only

TABLE 16c
CONTROL COST FOR VARIOUS MIST CONTROL SYSTEMS

VARIOUS TYPES OF ACID PLANTS
APPLIED TO

Process	Non Oleum Plants				Oleum Plants			
	Existing Plants		New Plants		Existing Plants		New Plants	
	50 T/D	750 T/D	50 T/D	750 T/D	50 T/D	750 T/D	50 T/D	750 T/D
3.1.1/1.1	\$.10	\$.08	\$.10	\$.02	\$.06	\$.04	\$.06	\$.04
3.1.1/1.2	.10	.07						
3.1.1/1.4		.11						
3.1.1/2.2			.10	.06				
3.1.2/1.1								
3.1.2/1.2	1.25	.33		.17		.28		
3.1.2/1.4		.45						
3.1.2/2.2			.90	.22			.18	
3.1.2/2.4				.31				
3.1.3/1.1		.15						
3.1.3/1.2	.45	.13		.10		.10		
3.1.3/1.4		.23						
3.1.3/2.2			.22	.05			.02	
3.1.3/2.4				.10			.05	
3.2.1/1.1		.26						
3.2.1/1.2	1.05	.25	1.05	.22	.90	.19	.22	.19
3.2.1/1.4		.33						
3.3.1/1.2		.36						
3.3.1/2.2			.36		N.A.		N.A.	

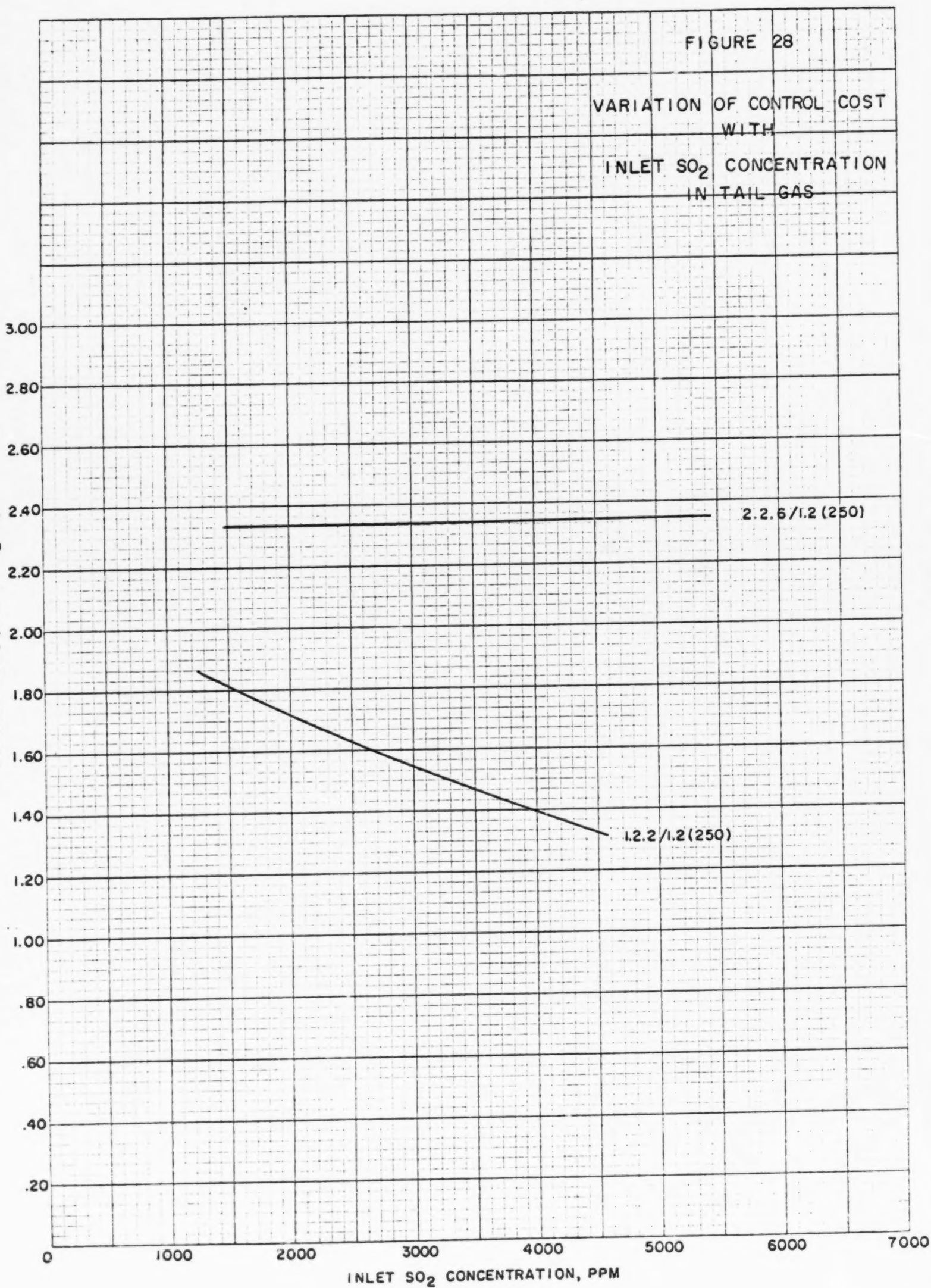
Variation of Control Cost with Inlet Concentration to the Control System

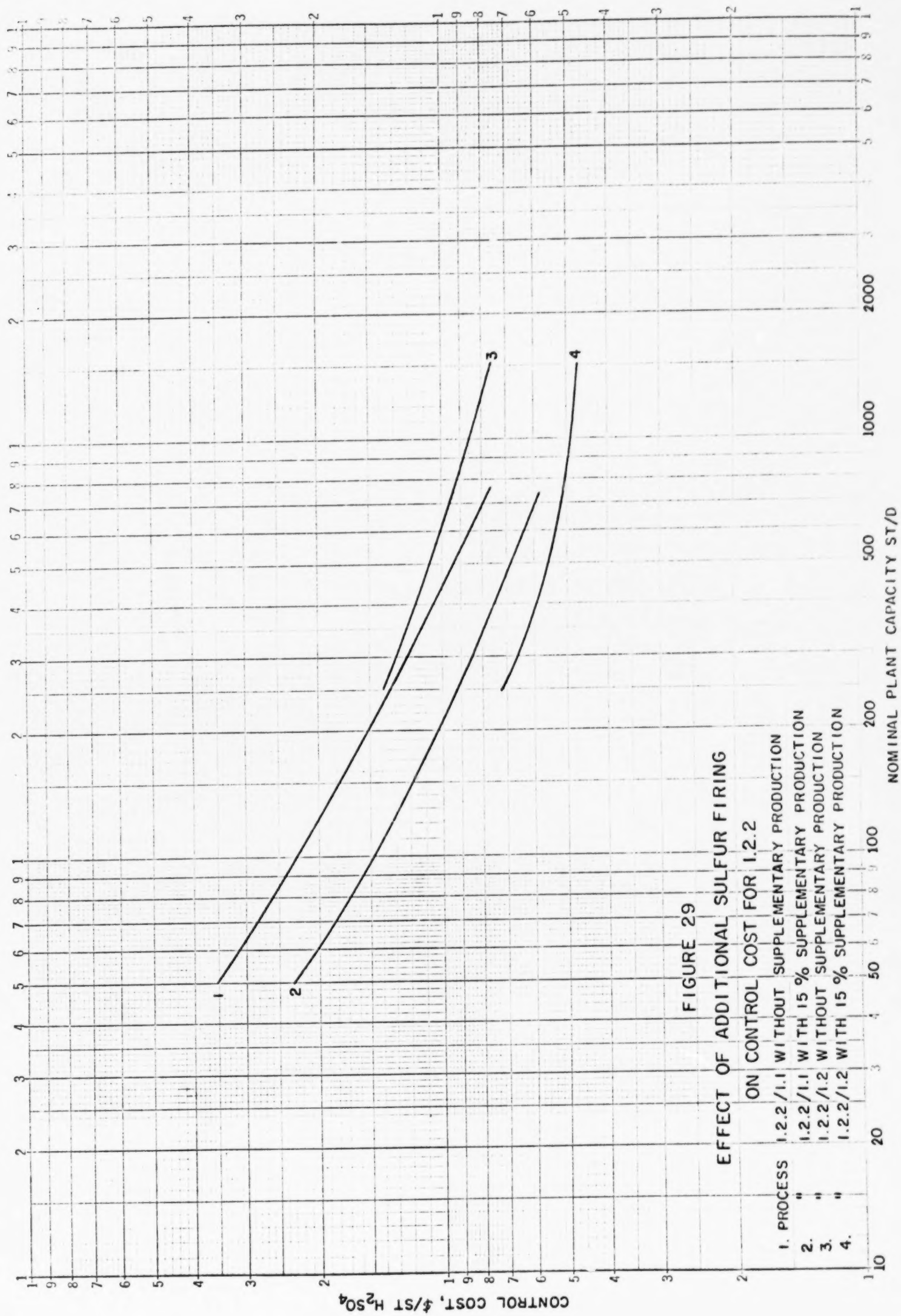
For add-on dual absorption systems the control cost is lower when applied to less efficient acid plants with high emissions of SO_2 . This occurs because the control effectiveness of these systems is fixed at about 500 ppm, so that with less efficient plants, for the same capital investment, more of the sulfur feed can be recovered as salable product, spreading the cost of operating the control system over a larger tonnage of product. This is illustrated in Figure 28.

From this it is obvious that after a control system of this type is added, it will be to the advantage of the acid plant operator to push a plant to its maximum capability, assuming that there is a market for the acid. This factor makes the control cost for process 1.2.2 superior to 1.2.1, as shown by Figure 29, which shows reduction in control cost for process 1.2.2 when burning additional sulfur to supplement production rather than gaining the necessary heat for dual absorption by reduction of steam production. The lower limit of control cost then depends upon the overdesign factors existing in the base plant. In some cases it may be possible to remove bottlenecks or make minor modifications in the base plant to further increase acid production and reduce control cost.

For tail gas scrubbing type processes, however, this does not appear to be the case, as shown on Figure 28 for process 2.2.6. Here the control cost remains constant with changes in inlet conditions. The value of additional acid recovery almost offset by additional capital costs. Other tail gas treating systems may give a slight advantage when pushed, depending upon the portion of the capital cost of the

CONTROL COST, \$/ST OF H₂SO₄





EFFECT OF ADDITIONAL SULFUR FIRING
 ON CONTROL COST FOR 1.2.2

- 1. PROCESS 1.2.2/1.1 WITHOUT SUPPLEMENTARY PRODUCTION
- 2. " 1.2.2/1.1 WITH 15 % SUPPLEMENTARY PRODUCTION
- 3. " 1.2.2/1.2 WITHOUT SUPPLEMENTARY PRODUCTION
- 4. " 1.2.2/1.2 WITH 15 % SUPPLEMENTARY PRODUCTION

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process represented by the SO_2 recovery section. Those which have a smaller portion of their cost in the recovery section are the ones which may have some advantage in operating with a higher SO_2 content in the tail gas.

Variation of Control Cost with Control Effectiveness

Generally, there appears little can be gained in operating a tail gas SO_2 recovery system below its maximum capability. An add-on dual absorption process control effectiveness can be improved slightly by making modifications to SO_2 concentration, air rate, catalyst quantity and converter temperature, but the change in control cost will be minimal. There would be very little advantage in operating a dual absorption system below its normal capacity. As can be seen from calculations of control costs in the appendix, the greatest portion of control cost is introduced by capital investment and requirements for additional plant operators where required. Very little is introduced by changes in utility requirements.

Tail gas treating systems if operated at a control effectiveness of 500 ppm rather than 200 ppm, for example, would save a little in capital cost, and slightly reduce utility costs by reducing circulation requirements in the absorption system. The saving would be a matter of a few cents per ton of acid in most cases. A possible exception may be a process such as 2.3.3 which produces a waste product. In this case a control system for a 1,500 T/D acid plant controlling from 4,000 ppm to 200 ppm has a control cost of \$.94. A system of control to 500 ppm would have a control cost of \$.89, a reduction of less than 6%. For a 50 T/D acid plant the reduction would be from \$6.00 to about \$5.80, a reduction of only 3%.

Variations of Control Cost with Plant Capacity

The control cost falls significantly as the size of acid plants to which a control system is applied increases. This is true for all systems studied. It is important, however, to note that the rate at which the control cost decreases is not the same for all systems. This is illustrated by Figure 30.

Systems such as resin adsorption (2.2.29) and lime scrubbing (2.3.3) are lowest in control cost among tail gas treating systems for small plants, but more costly relative to other systems when applied to large plants. This is due to cost factors in these processes which increase in direct proportion to plant capacity at a given emission level such as resin volume and the quantity of lime consumed.

By this illustration we conclude that processes which are potentially attractive for application to small plants may be less attractive for large acid plants, and vice versa.

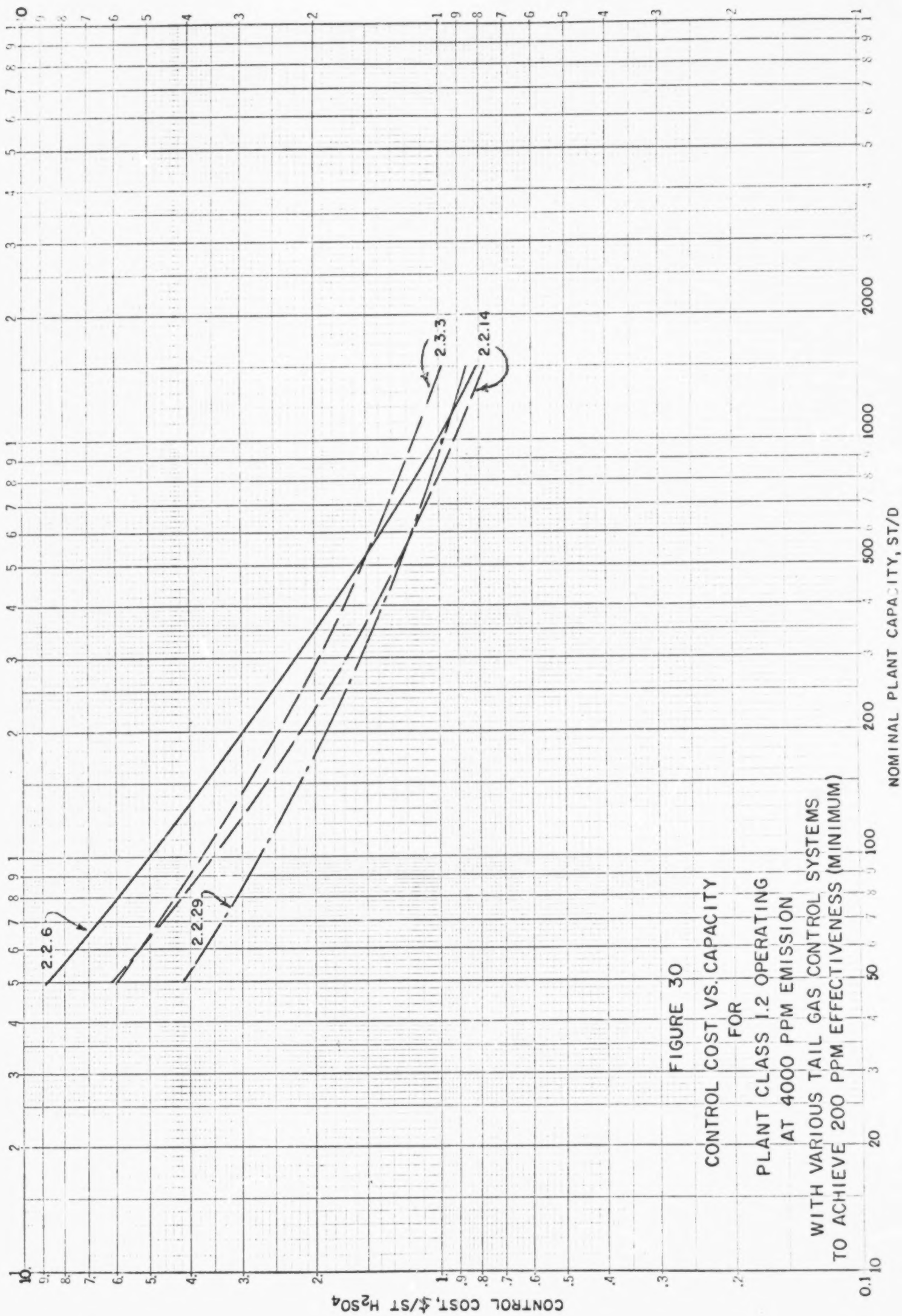


FIGURE 30
CONTROL COST VS. CAPACITY
FOR
PLANT CLASS 1.2 OPERATING
AT 4000 PPM EMISSION
WITH VARIOUS TAIL GAS CONTROL SYSTEMS
TO ACHIEVE 200 PPM EFFECTIVENESS (MINIMUM)

Control Costs for New and Existing Acid Plants

The control cost for a new dual absorption plant is lower than that for an existing plant converted to dual absorption. Some reasons for this were discussed previously.

For tail gas recovery systems the cost may be slightly less for an all new installation. Differences would be increased by lack of space at an existing unit, which could make application to an existing unit considerably more expensive.

For mist control, however, installation in an existing unit can make a significant difference in the control cost, as shown below; for 250 T/D plants, Classes 1.2 and 2.2, producing no oleum:-

<u>System</u>		<u>Control Cost</u> <u>\$/Ton for 2.2</u>	<u>Control Cost</u> <u>\$/Ton for 1.2</u>
3.1.1	Dual Mist Pads	\$.06	\$.07
3.1.2	Tubular Type	.22	.33
3.1.3	Panel Type	.05	.13

Special Situations

Many factors peculiar to a plant or location can affect the control cost of any system; however, it is not felt that there are any acid plants to which it would be technically impossible to apply some type of control system. There may be some, however, which would find the control cost so high that the plant could not be operated economically, such as small plants, congested plants, and marginal plants.

Some situations require a special evaluation, such as the following example which is illustrated by Table 17. Assume an acid plant of four producing units, two of which are 150 T/D class 1.1 plants, one is a 300 T/D class 1.2 plant and the fourth is a 600 T/D class 1.2 plant.

To apply process 2.2.6, employing MgO scrubbing with SO₂ recovery would require 4 scrubber sections and one recovery section capable of handling the combined capacity of the four acid units. This would also add one operator. The production cost per ton of acid for this combination is \$12.68.

To apply four separate add-on dual absorption systems of type 1.2.1 would require 4 individual designs, but add no operators. The production cost in this case is \$12.76, virtually the same, though for a single unit the 1.2.1 system results in a far lower control cost than 2.2.6. This illustrates the possible advantage of a central recovery system. It is also possible to install a central add-on dual absorption in certain situations. The dual absorption would be somewhat different from these described here, however.

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Special conditions affecting a particular plant can radically affect the control costs shown here. Some of these might be a readily available low cost supply of a required chemical, a unique need for a by-product that could be produced, existence of sufficient operators, and many more. Detrimental conditions may be lack of space, unusual construction problems, costly startup or operating costs related to use of a process which has not been satisfactorily demonstrated, waste material disposal problems, among others. This work has attempted to place control costs on a comparable basis.

TABLE 17

COMPARISON OF ACID PRODUCTION COSTS
FOR
MULTI-UNIT PLANT WITH
CONTROL SYSTEMS 1.2.1 AND 2.2.6

NOTE: Plant consists of 4 units; 2 class 1.1, 150 T/D each,
1 class 1.2, 300 T/D and 1 class 1.2, 600 T/D for a
total daily production of 1,200 T/D.

Process	2.2.6/1.1, 1.2 (1200)	1.2.1/1.1, 1.2 (1200)
Nominal Capacity	1,200 T/D	1,200 T/D
Production Rate	1,254 T/D	1,250 T/D
Conversion Rate	99.775 %	99.5 %
Initial Investment	\$6,215,000	\$6,825,000
Book Value	3,295,000	3,905,000
Raw Material and Utilities		
Sulfur	\$3,390,000	\$3,390,000
Elec. Power	211,000	277,000
Cooling Water	124,200	144,000
Process Water	1,650	1,650
B.F. Water	28,900	23,700
Steam	- 322,500	- 260,000
Fuel Oil	150,300	
MgO	53,800	
Operating Expenses		
Labor	237,500	190,000
Supervision	63,300	63,300
Maintenance (4%)	247,500	273,000
Overhead @ 70% of Above	384,000	368,500
Indirect Costs		
Depreciation 10%)	576,500	633,000
Interest 7-1/2%)		
Taxes and Insurance (1-1/2%)	93,200	102,300
Annual Operating Cost	\$5,239,350	\$5,256,450
T/Y Acid Production	413,300	412,000
Production Cost/T	\$ 12.68	\$ 12.76

NOTE: Class 1.1 Units Assumed 5,000 ppm Emission
Class 1.2 Units Assumed 4,000 ppm Emission

Economic Comparison of Control Systems

The technically ideal control system would also be ideal from the economic standpoint if it did not add to the cost of producing acid, but again, such a system does not presently exist. No one of the systems studied in this report produces the lowest control cost for all sizes and types of acid plants under all conditions.

Add on dual absorption systems may also require the addition of mist control equipment to achieve complete control if none exists on the base plant. In this instance, the cost of mist control must be added to the cost for SO₂ control. Of the add on dual absorption systems 1.2.2 seems to offer SO₂ control at minimum cost, especially if the base plant is capable of additional acid capacity as a result of inclusion of 1.2.2. This is true over the entire existing capacity range for single units.

For tail gas recovery processes, however, the selection is not as clear cut. Generally, for small plants the simplest systems, 2.3.3 and 2.2.29, produce minimum control cost. For larger plants 2.2.6 and 2.2.14 appear most attractive. There is an intermediate area where the control costs for these four above mentioned systems are approximately equal.

Mist control systems offer several choices at approximately equal control cost for equivalent removals. The control cost for the simpler systems are so small that it will make little difference which is selected.

VI
ECONOMIC EFFECTS OF
RECOVERED SULFUR VALUE UTILIZATION

There has been considerable effort expended in developing systems for control of atmospheric emissions from sources which emit large quantities of SO_2 , particularly fossil fuel power plants and smelters. When a significant number of these processes become operational new sources of sulfur will appear. This sulfur may take the form of elemental sulfur, sulfur dioxide, sulfuric acid or a sulfur containing salt for sale (from which SO_2 may be readily recovered, such as MgSO_3).

If these sources become available they will compete with sulfur for the sulfuric acid market. They will not compete with acid sludge, H_2S or SO_2 from smelting operations, since these materials are already recovered waste products which must be disposed of in some manner.

The only form which the recovered sulfur may take, which is not presently used as a raw material for sulfuric acid, is 100% SO_2 . In this section several methods of using SO_2 in the H_2SO_4 industry are discussed.

There has been surprisingly little interest in the recovery of SO_2 from either smelter gas or power plant stacks as liquid SO_2 . If sulfuric acid cannot be made on the spot -- and on the whole power plants do not want to make it -- most operators would prefer to make sulfur, or if that proves impossible, magnesium sulfite or some other easily transportable solid. It is probably correct to say that any recovery plant in operation at this time produces either sulfuric acid or sulfur.

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The objections usually raised to SO_2 are the problems of storage and transport. Obviously, sulfur has great advantage here, being a non-toxic safe solid or only half the weight of SO_2 , but to reduce SO_2 to sulfur uses relatively expensive reducing agents as well as heat.

Liquid SO_2 would be lighter to transport than sulfuric acid (only about 2/3 the weight) and would not be much more difficult. Liquid ammonia and LPG are transported in large quantities at higher pressures than are necessary for SO_2 .

Liquid SO_2 can replace a proportion of the sulfur in any sulfur burning acid plant without significant modification. It can also be fed to a roaster gas plant -- but if ore-roasting is the main factor this would not be acceptable, since roaster operation would have to be reduced to avoid excess SO_2 . This is probably the way any use of liquid SO_2 would start. The two H_2SO_4 processes designed to use liquid SO_2 described here are of special interest from a pollution standpoint. The total recycle oxygen process has virtually no effluent and the partial recycle air process allows only 1/3rd of the SO_2 into the atmosphere compared to a comparable sulfur burning plant. We believe, therefore, that these represent a significant advance in reducing pollution. It now only remains to find an acceptable SO_2 recovery process. Further development of some of those described may provide the answer.

Utilization of SO_2 in existing plants would curtail steam production, which might not be desirable.

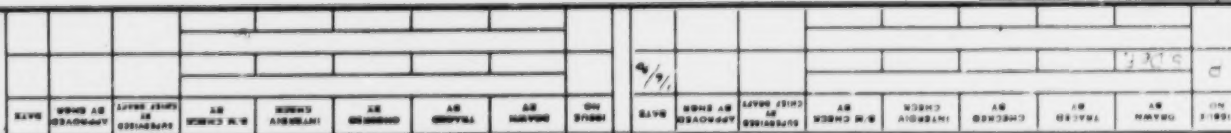
It is unlikely that existing acid plants could be economically converted to use 100% SO_2 .

Partial Recycle Air Process (PRAP)

The Partial Recycle Air Process (PRAP) utilizes tonnage SO_2 (100% SO_2) and air for the manufacture of 98% sulfuric acid. The main technical advantage of the process from an air pollution standpoint is that tail gas emission is about one third the amount from a standard sulfur burning plant, hence the SO_2 discharge is one third also. This is due to the fact that two out of three moles of O_2 used up in a contact sulfuric plant go for the oxidation of sulfur to sulfur dioxide, but when sulfur is available as SO_2 the only O_2 required is to convert SO_2 to SO_3 . As a result, no sulfur furnace, waste heat boiler or associated equipment are required and the drying tower is designed for one third the duty of a conventional contact plant. The converter boiler and economizer are replaced by a series of heat exchangers designed to reheat the converter feed gas mixture, but otherwise the contact and acid making sections of the plant remain unchanged.

The converter feed gas consists of 8% SO_2 , 13% O_2 and 79% N_2 . A 98% conversion is achieved in four catalyst stages, and the SO_3 rich product gas is fed to the 98% absorption tower where the SO_3 is absorbed. The tower off-gas, being rich in oxygen, is split into recycle and purge (stack gas) streams. The split is determined by the amount of oxygen that has to be made up in the recycle gas. The stack gas represents a nitrogen purge equal to the amount of nitrogen in the feed air to the system. The recycle stream is enriched by SO_2 and air in order to maintain the original converter feed gas composition and the cycle is repeated.

The stack gas, despite containing approximately 2,000 ppm of SO_2 , has about one third the quantitative SO_2 emission of a comparable



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single absorption sulfur burning unit, or in terms of conversion efficiency based on input and output of SO_2 , PRAP achieves 99.3% conversion, a notable improvement over 98%.

This process, additionally, uses conventional sulfuric acid technology and could be built on commercial scale without piloting.

In addition to the technical advantages cited above, the estimated capital investment required for PRAP is 10-20% lower than for a conventional sulfur burning plant of class 2.2. While an inability to produce steam as a by-product may be a disadvantage in some instances, PRAP appears to have distinct economic advantages if tonnage SO_2 becomes available.

Table 18 shows the production cost for a 500 T/D PRAP plant. Compared to a conventional sulfur burning plant of class 2.2, the production cost per ton of acid is reduced by \$.50, assuming a cost of \$12.50/ton for SO_2 .

TABLE 18
ACID PRODUCTION COST FOR
PARTIAL RE CYCLE AIR PROCESS

Process	P. R. A. P.
Nominal Capacity	500 ST/D
Production Rate	500 ST/D
Conversion Rate	99.3 %
Initial Investment	\$1,400,000
Book Value	1,400,000
Raw Material and Utilities	
S as SO ₂	\$1,360,000
Elec. Power	62,700
Cooling Water	23,800
Process Water	560
Operating Expenses	
Labor	47,500
Supervision	21,100
Maintenance (4%)	56,000
Overhead @ 70% of Above	87,200
Indirect Costs	
Depreciation 10%)	245,000
Interest 7-1/2%)	
Taxes and Insurance (1-1/2%)	21,000
Annual Operating Cost	\$1,924,860
T/Y Acid Production	165,000
Production Cost/T	\$ 11.65

Total Recycle Oxygen Process (T.R.O.P.)

This is a "pollution free" sulfuric acid process which utilizes liquid 100% SO_2 and 99.5% O_2 as raw materials. The principal advantage of the process being that essentially no tail gas is emitted as a result of using O_2 instead of air.

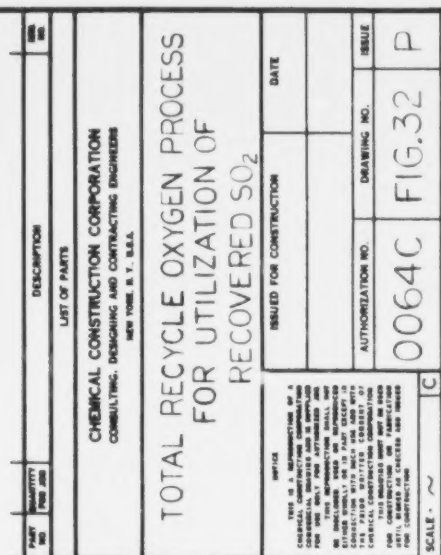
A level of inerts (N_2 and rare gases) is maintained in the process loop to control temperatures and act as a heat carrier. The process loop consists of the total recycle of SO_2 and O_2 enriched absorption tower off gases back to the converter, the subsequent conversion of SO_2 to SO_3 , then the absorption of SO_3 followed by re-enrichment and so forth.

Oxygen requirements may be met either by importing "over the fence" or installing an air separation plant. An integrated TROP - Air Separation Facility could utilize a steam driven air compressor with 56% of the energy being supplied by the waste heat generated by the SO_2 to SO_3 reaction.

The battery limits TROP unit is very simple and basically consists of the following items; as depicted in Figure 32:-

- two-stage converter
- converter waste-heat boiler
- heat exchanger
- absorption tower
- acid cooling system
- acid pump tank and pump
- recycle blower

The economics of a 500 ST/D H_2SO_4 production facility consisting of a TROP unit and an 82 ST/D Air Separation plant yielded an estimated

[illegible]

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capital cost of \$2,130,000 and assuming a raw material cost of \$12.5/ton SO_2 the cost of producing H_2SO_4 is estimated at \$12.75/ton, as shown in Table 19.

The T. R. O. P. unit requires a small purge stream in order to remove inerts equivalent to the impurities brought in with the oxygen. For a 500 STD plant the purge is approximately 7 SCFM of 91.5% N_2 and rare gases, 7.5% O_2 and 1% SO_2 ; i. e. 0.07 SCFM SO_2 is emitted to the atmosphere or may be reclaimed by any appropriate means. It is worthwhile to compare this purge with the tail gas of a modern 500 ST/D sulfur burning 10% SO_2 dual absorption plant, where the tail gas is approximately 21,600 SCFM containing 500 ppm SO_2 , the SO_2 emission in this latter case is 10.8 SCFM or approximately 154 times the amount of SO_2 in the T. R. O. P. purge stream. The overall T. R. O. P. unit SO_2 efficiency is 99.997%.

This process, as in the case for P. R. A. P., uses conventional sulfuric acid technology and could be built on commercial scale without piloting.

TABLE 19
ACID PRODUCTION COST
FOR
TOTAL RECYCLE OXYGEN PROCESS

Process	T. R. O. P.
Nominal Capacity	500 ST/D
Production Rate	500 ST/D
Conversion Rate	~100 %
Initial Investment	\$2,130,000
Book Value	2,130,000
Raw Material and Utilities	
S as SO ₂	\$1,350,000
Elec. Power	45,400
Cooling Water	26,200
Process Water	670
B.F. Water	2,370
Steam	14,050
Operating Expenses	
Labor	47,500
Supervision	21,100
Maintenance (4%)	85,000
Overhead @ 70% of Above	107,500
Indirect Costs	
Depreciation 10%)	373,000
Interest 7-1/2%)	
Taxes and Insurance (1-1/2%)	31,930
Annual Operating Cost	\$2,104,700
T/Y Acid Production	165,000
Production Cost/T	\$ 12.75

VII
RECOMMENDATIONS

A. TECHNOLOGY LIMITATIONS

Applications

It is not likely that there is any contact acid plant in the U.S. to which a satisfactory emission control system could not be applied. It is doubtful, however, that all plants could be operated economically with control systems, and such decisions would necessarily have to be made on an individual basis. If some plants were forced to close because the cost of control was too high, older, smaller plants with restricted choice as to possible control methods would probably be most affected. Timing is also important. Certainly, the next few years will see improvements in effectiveness and cost as new systems are developed which may be used to advantage by marginal plants.

To the advantage of older, less efficient plants, a number of control methods that are presently available or potentially feasible are less costly to apply to such units.

Control Effectiveness

A control effectiveness of 2,000 ppm (overall) is not too difficult to reach with minor modifications to plant operation and minimum capital expenditure. It is very likely, however, that production will be somewhat curtailed and production costs per ton of acid would increase as a result of such changes.

Presently available technology will permit reducing emissions to less than 500 ppm SO_2 via the dual absorption route for those plants which can accommodate the necessary additional equipment. For control effectiveness levels of 100 or 200 ppm, however, little is available which is commercially proven. As control effectiveness becomes greater, the number of potential choices and their degree of development decreases rapidly. These are the areas where further development efforts need to be concentrated.

The effectiveness of various systems will depend to a great extent upon how they are operated, though limitations do exist. Dual absorption processes are limited by operating plant conditions and SO_2 - SO_3 equilibrium at these conditions, which makes 500 ppm a practical level, although 200-300 ppm is possible with careful operation.

Tail gas recovery systems will depend upon the inlet SO_2 concentration in many cases to determine effectiveness. Chemico has been able to achieve 95% removal in a venturi scrubber on a continuous basis from a power plant stack with inlet concentrations of about 1,500 ppm; higher efficiencies may be feasible. Other devices such as packed towers can be equally effective. With 95% as the removal efficiency, to reach 500 ppm effectiveness, the inlet SO_2 concentration may be as high as 10,000 ppm, but a regulation requiring 100 ppm control effectiveness will limit inlet concentration to 2,000 ppm. Increased absorption efficiency or multiple absorption stages may improve this.

Tail gas recovery systems which utilize resin adsorption or molecular sieves reportedly can achieve a control effectiveness of near zero. They have yet to be demonstrated on a pilot or commercial scale, however.

Acid mist control systems which are capable of mist control well below 3 mg/SCF even for sub-micron mist from oleum plants are in commercial operation. Regulations governing mist concentrations at ground level vary widely, and suitability of systems should be determined on an individual basis. In some areas 3 mg/SCF with good dispersion may be satisfactory. In others it is not.

Oleum Plants and Mist Control

Oleum plants probably present the most acid mist control problems since they emit more and finer mist than 98% acid plants. They will probably be limited to a system capable of controlling SO_2 , SO_3 and mist, or a combination of dual absorption and one of the most effective mist control systems, as 3.1.2 or 3.2.1.

Space Limitations

Generally, wet gas acid plants will tend to be more congested than sulfur plants, and older plants more congested than new plants. In the first place, wet gas plants are more complex; also, they are often a secondary facility, supporting refinery operations or controlling emission or disposal problems themselves, and as such may be squeezed in wherever space could be found.

Older plants have been modified by the owners in various ways and other facilities have been built nearby to occupy any extra space available. These factors will all contribute to the difficulty of fitting in a control system.

Process Development

It should be stressed that many of the systems discussed, particularly for recovery of SO_2 , SO_3 and mist from tail gases, are not fully developed. For the purposes of this study the control costs were developed on the assumption that the control systems as described in the report will perform as expected. Further development may prove the systems better or worse, and more or less costly than the figures given on the subsequent pages.

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Class 1.1 Acid Plants

Based on the calculations in Parts IV and V, a class 1.1 acid plant can control to 500 ppm with the following systems and at the following control costs for a 250 T/D unit:

<u>Process</u>	<u>Control Cost \$/Ton H_2SO_4-</u>
1.2.1	\$1.44
1.2.2	\$.92
2.1.1	\$3.13
2.2.6	\$2.71
2.2.8	\$2.84
2.2.14	\$1.98
2.2.22	Unknown
2.2.28	\$2.91
2.2.29	\$1.50
2.3.3	\$2.33
2.4.5	\$2.63
2.4.6	\$3.50

For control to 100 ppm, at normal emission levels, shown in Part III:-

<u>Process</u>	<u>Control Cost, \$/Ton of H_2SO_4-</u>
2.2.29	\$1.50

A combination of 1.2.1 or 1.2.2 with any of the 2.x.x series could also achieve this result. This combination would be very expensive and not a likely commercial venture.

From the above it becomes evident that there is very little difference in control cost to reach effectiveness levels of 500 ppm vs. 100 ppm.

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Class 1.2 Acid Plants

The following systems can be expected to achieve a 500 ppm control effectiveness with class 1.2 acid plants at the control costs listed for 250 T/D plants:-

<u>Process</u>	<u>Control Cost, \$/Ton of H_2SO_4-</u>
1.2.1	\$1.48
1.2.2	\$.73 to \$1.39
2.1.1	\$3.05
2.2.6	\$2.51
2.2.8	\$2.73
2.2.14	\$1.88
2.2.22	Unknown
2.2.28	\$2.96
2.2.29	\$1.63
2.3.3	\$2.14
2.4.5	\$2.52
2.4.6	\$3.33

For control to 100 ppm at normal emission levels shown in Part III, the following would be applicable. Depending upon present emission levels, it may also be necessary to also make adjustments as described for 1.3.4. The cost for these adjustments should be minor; and additive to the following:-

<u>Process</u>	<u>Control Cost, \$/Ton H_2SO_4-</u>
2.1.1	\$3.05
2.2.6	\$2.51
2.2.8	\$2.73
2.2.14	\$1.88
2.2.29	\$1.63
2.3.3	\$2.15
2.4.5	\$2.52
2.4.6	\$3.33

Class 1.3 and 1.4 Acid Plants

For control to 500 ppm the following systems may be expected to perform satisfactorily with wet gas plants, although control cost will vary widely with the raw material used. Control costs are generally somewhat higher than for classes 1.1 and 1.2, but the relative cost positions of the various systems should be about the same. Those given as examples are for smelter or roaster gas plants of class 1.4.

This type was selected because their tail gas flow is between that of H₂S plants and Copper Converter gas plants. The effect of inlet concentration and flow rate on control cost and capital cost is discussed in Part V. The relative flow rates for various types of wet gas plants are given in Part IV.

<u>Process</u>	<u>Control Cost, \$/Ton of H₂SO₄-</u>
1.2.3	\$2.31
2.1.1	*
2.2.6	\$2.92
2.2.8	\$2.87
2.2.14	\$2.67
2.2.22	*
2.2.28	*
2.2.29	*
2.3.3	\$2.48
2.4.5	\$2.95
2.4.6	\$3.70

For control to 100 ppm the following systems could be applied, together with some of the process modifications outlined in 1.3.4 for class 1.3 or 1.4 plants:-

* Not Calculated

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<u>Process</u>	<u>Control Cost, \$/Ton of H₂SO₄-</u>
2.1.1	*
2.2.6	\$2.92
2.2.8	\$2.87
2.2.14	\$2.67
2.2.29	*
2.3.3	\$2.48
2.4.5	\$2.95
2.4.6	\$3.70

For class 1.3 plants with high initial emission levels process 2.2.29 may be the only suitable process, or a combination of 1.2.3 with one of the above systems. Modifications suggested in 1.3.4 would be of little help because of the magnitude of adjustments required in such a case. Systems of the 2.x.x group may also be applicable with multiple absorption stages.

* Not Calculated

B. DEVELOPMENT PROGRAMS

It is desirable to reduce some of the limitations of existing systems, to make processes in the development stage more feasible, to improve the capabilities of processes both in number of applications and in control effectiveness. We have, in preparing this report, surveyed many potential processes which may be applicable to sulfuric acid plants. Many of these processes appear to have common problems whose solution will improve their usefulness. As NAPCA is interested in commercialization of effective control systems, we have suggested several areas where new or continued programs can help in development of as many potential systems as possible which may be particularly applicable to sulfuric acid plants. Development of two systems which, if developed, seem to have the characteristics which would make them attractive for acid plant emission control is also recommended. These programs are listed below in a suggested order of priority, and are further described on subsequent pages.

1. Resin or Molecular Sieve Adsorbents.
2. Oxidation Inhibitors.
3. Plume Dispersion for Scrubbed Stack Gases.
4. Development of Process 2.3.1.
5. Development of Process 1.3.2.
6. Chamber Acid Plant Emission Control.

Resin or Molecular Sieve Adsorbents

This is a relatively untouched area until recently for pollution control. For sulfuric acid plants where tail gas is clean and the gas flows and SO_2 concentrations are relatively low this type of system could prove economical, simple, compact as well as very effective for almost all types of plants. As this appears to offer the ultimate in SO_2 control, its effectiveness makes it the first for consideration.

Desirable characteristics of these materials include:-

- . High SO_2 loading at partial pressures and temperatures of SO_2 normally encountered (.001 to .020 atm.)
- . Selectivity for SO_2 high with respect to H_2O
- . Long life (over 2 years, preferably)
- . Stable, unaffected by SO_3 or H_2SO_4
- . Low pressure drop
- . Regenerates at low temperature

If a material can handle SO_2 and SO_3 equally well, this is advantageous. If not, then the following would need study:-

- . SO_3 loading at partial pressures normally encountered (.00005 to .01 atm.)
- . Rate of oxidation of SO_2 to SO_3 at oxygen partial pressures between .04 and 0.2 atm.
- . Effect of water vapor on SO_2 - SO_3 oxidation rate
- . Method for removal of SO_3 prior to SO_2 removal

If an evaluation shows the basic characteristics of an absorbant to be attractive, if the material is easily produced and not excessively expensive, then a development program to determine the answers to

these questions would be desirable. For some applications selectivity with respect to CO, CO₂ and nitrogen oxides may also be important.

After determination of design characteristics and laboratory testing with a synthesized tail gas, a pilot unit prototype would be required to determine regeneration cycles and material life under actual conditions at a sulfuric acid plant using a portion of the tail gas stream.

Oxidation Inhibitors

Many of the tail gas treating systems for SO_2 control utilize sulfite and bisulfite salts solutions as a scrubbing medium. In many of these systems there is a tendency for oxidation to form sulfates which are not readily regenerable. For these processes in which a minimum of sulfate formation is desirable, introduction of an oxidation inhibitor may be effective. The formation of sulfate when treating H_2SO_4 plant tail gases is more serious than with other stack gases due to the presence of 10 to 12% oxygen in the acid plant tail gas stream. Development of an effective inhibitor can be an important step in reducing the control cost for several systems presently being tested, and is suggested as a second priority. This development could be done before or in parallel with testing of prototype systems. Prior development, however, may show that in some one system oxidation may be easier to control than in others. This would serve as a guide in selecting systems for prototype testing.

The use of oxidation inhibitors to prevent oxidation of sulfite and bisulfite salts would apply to process 2.1.1, 2.2.6, 2.2.8, 2.2.14, 2.4.5 and 2.4.6. The use of an oxidation inhibitor would be important for these processes if oxidation is excessive. The potential for oxidation is present with the oxygen content of the tail gas being about 10%. O_2 would dissolve in the SO_2 absorbing solutions.

Several oxidation inhibitors have been reported in the literature: hydroquinone,⁽¹⁾⁽²⁾ p-aminophenol,⁽³⁾⁽⁴⁾ quinol,⁽⁵⁾ glycine,⁽⁶⁾ etc., which were effective under bench scale conditions. In addition, there are

(Footnotes - See next page)

oxidation retardants such as stannous chloride⁽⁷⁾ and mannitol⁽⁸⁾ which may also be applicable.

Going through the processes one by one; process 2.1.1 requires an inhibitor to prevent oxidation of sodium sulfite to sulfate. Process 2.2.6 requires that oxidation of magnesium sulfite to sulfate should not be excessive. Similarly, potassium sulfite-bisulfite, ammonium sulfite-bisulfite and methyl ammonium sulfite-bisulfite absorbing solutions should not oxidize inordinately. For process 2.4.6 calcium sulfite oxidation should be minimized.

Besides direct oxidation there are substances which promote oxidation. Examples of these are ferrous and copper sulfates, and sodium nitrite. Small amounts of copper and iron can dissolve into the absorption system from the absorbants used as well as from materials of

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I. & E. Chem. - Vol 30. No. 1 - Jan., 1938
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"Oxidation of CaSO_3 in the Process of Scrubbing SO_2
From Flue Gases"³
Zhur Priklad Khim. - 33, 1708-1714 (1960)

construction. In addition, particulate matter such as slurry solids can act as catalysts. The pH of the absorbing solution can also accelerate oxidation, where, for instance, under acid conditions either oxygen becomes more reactive or certain oxidation catalysts such as FeSO_4 become more soluble. There are also reagents such as manganous hydroxide, which can promote oxidation in alkaline solutions.

Solution to this problem of oxidation would, therefore, require piloting the absorption stages and other parts of the processes where sulfite and bisulfite salts in the liquid phase are heated above ambient temperatures. Piloting should be done under steady-state conditions with actual tail gases, and with reagents and materials of construction that would be used in full-sized systems after some laboratory screening work where conditions can be varied.

Plume Dispersion for Scrubbed Stack Gases

As brought out earlier, liquid phase absorption of SO_2 cools and saturates the tail gases. Two suggested methods for maintaining effective stack heights and preventing any rain-out of condensate are direct heating of the cleaned gases or partial heating plus increasing the velocity of the exiting gas. As a guide in determining the effectiveness of this type of process and others as well, it is important to analyze the effects of the many factors that determine the relationship between stack emission and ground level concentration for both SO_2 and acid mist. Since acid plant tail gases are relatively cool compared with many others, this is particularly important for acid plants. Such a study would also be valuable in helping to define emission standards for other types of systems and other pollutants, and is suggested as a third priority.

Mathematical studies should be made relating the many variables of plume dispersion with ground level concentrations of SO_2 . This would show the effectiveness of increasing gas velocity and temperature to significantly lower ground level concentrations.

The first part of the study should determine which of the many dispersion formulas would be most suitable for scrubbed tail gas emissions. At least two dissimilar formulas should be selected.

A second important parameter is the rate of SO_2 emission (i. e., lbs. /min.) in the scrubbed gas. This is determined by the plant size, or CFM of exiting gas, and the SO_2 concentration.

Another important set of variables are the cleaned gas velocities and densities which determine the rise of the plume above the stack, which in turn determines the effective stack heights. Gas velocities and densities (or temperatures) should include values before and after heating and increasing the velocity of the cleaned gas. Ambient air temperature can be set at a typical summertime reading.

In addition to the intrinsic properties of the cleaned gases, geographic and geometric factors should also be taken into account. These include physical stack heights and horizontal distances downwind from the source to a point on the ground.

The more difficult variables to establish are meteorological and the topographic, the latter of which adds to the complexity of plume diffusion. The stability of the atmosphere is expressed in certain dispersion formulas as an exponent of the distance downwind of the source. Three atmospheric stability factors have been shown but only two have been chosen for these calculations, most stable (inversion) and average. The elements of terrain such as buildings, mountains, shoreline, trees and valleys, which cause turbulence or channeling of plumes, are too variate for any numbers to be established. Acid plants, however, are usually in non-urban areas so the above turbulence factors may not be critical except for plant locations in valley areas. In this case maximum atmospheric stability would probably be indicative of plume dispersion.

Wind velocity, another important meteorological variable, is inversely proportional to contaminant concentrations. A suitable range of velocities should be selected.

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From the above the number of variables for each category is tentatively set as follows for the calculation of groundlevel SO₂ concentrations:

	<u>Number</u>
Dispersion Formulas	2
Plant Sizes, T/D: 100, 500, 1, 500	3
SO ₂ Concentrations, Scrubbed Gas: 50, 100, 200, 500 ppm	4
Scrubbed Gas Velocities: one typical, two increased	3
Gas Densities or Temperatures: one at typical saturation, two above saturation (heating gas)	3
Ambient Air Density - at one temperature	1
Atmospheric Stability - Exponent for more stable and average conditions	2
Stack Heights: 20, 50, 100, 250 Ft.	4
Distances from Source: 0.1, 0.5, 1.0, 2.0 mi.	4
Wind Velocities: Low and Moderate	<u>2</u>
Total SO ₂ Groundlevel Values	13,824

After completion of the mathematical phase it may be desirable to measure each of the factors at various locations and condtions to check the validity of the theoretical calculations.

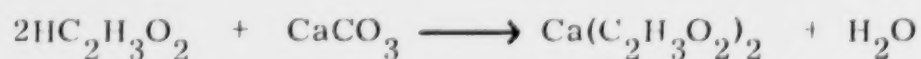
Development of Process 2.3.1

This process was chosen because of its similarity to process 2.3.3 which is already potentially attractive for SO₂ control of sulfuric acid plant tail gases. Process 2.3.3 is simple, effective and well developed; process 2.3.1 is undeveloped, but uses CaCO₃ in place of CaO. CaCO₃ is much less expensive than CaO, and with successful development 2.3.1 could be a useful control system, approaching dual absorption in control cost while having a greater control effectiveness.

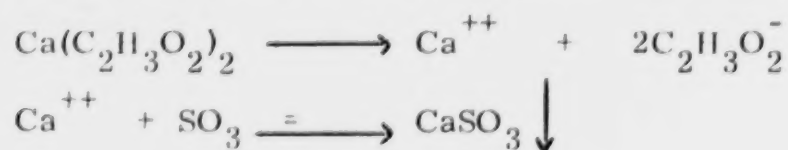
The objective is to increase SO₂ absorption and alkali consumption efficiency of systems utilizing limestone or dolomite slurries for the absorption of SO₂. This is to be achieved by adding an agent which will increase the solubilities of the calcium and magnesium carbonates in these minerals, providing greater concentration of dissolved reactant. In addition, many limestones and dolomites which have been classified as ineffective for the absorption of SO₂ may then be usable.

Fair to middling absorption and alkali consumption efficiencies are effected by many limestones and dolomites due to low solubility of the calcium and magnesium carbonates (in water). The presence of impurities in these minerals may inhibit the reaction of a substantial portion of the carbonate with sulfurous acid.

Acetic acid reacts with carbonate as follows:-



The acetate ionizes providing a greater reactant concentration:-



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Therefore, when SO_2 is absorbed the acetic acid is regenerated:-



The free acid formed in the absorption stage would then dissolve carbonate mineral in its immediate presence. The mineral would be finely ground and completely dispersed throughout the slurry. Maximum acetic acid concentrations developed during absorption would be below the point at which there would be significant vaporization into the flue.

The reagent costs for the Acetic Acid-Limestone process are estimated to be about one-half of that for the Lime Process (2.2.3). For each ton of lime, 1.9 tons of limestone would be required plus 0.0123 tons of acetic acid. SO_2 absorption efficiency would probably be lower for limestone, 90% instead of 95%, but alkali consumption efficiency may be about the same (90%).

Development of Process 1.3.2

Introduction of ozone to promote the oxidation of SO_2 to SO_3 is very different from most of the systems surveyed. Chemico has done some testing in this area, and results are sufficiently encouraging to recommend additional study. The system is very simple and adaptable to all acid plants. Control cost could be as low as \$.07 for a 250 T/D plant at an effectiveness of 500 ppm of SO_2 .

It is suggested that bench scale and test work at an acid plant site be done with regard to the oxidation of the SO_2 with ozone remaining after the catalytic oxidation step. Ozone would enter the system between the economizer and the 98% absorption tower to oxidize the SO_2 in the SO_3 - SO_2 - O_2 - N_2 gas mixture. The SO_2 concentration in the tail gas would then be reduced to an amount at which emissions to the outer air would no longer be a problem.

The objective would be to have very efficient oxidation, that is one mole of ozone oxidizing several moles of SO_2 . Ozone may react most rapidly with the SO_3 to form an unstable compound which, upon decomposing, could activate many times its number of SO_2 and O_2 molecules. Another possibility is that ozone would decompose with such vigor that it could activate SO_2 and O_2 in its immediate vicinity. A relatively small ozone generator would be required with the ozone containing gas entering the system evenly dispersed across its entrance point.

The estimated cost of a system recovering 6.8 T/D of 98% acid from a 250 T/D acid plant is listed in Table 19. The 6.8 T/D of acid is equivalent to 90% removal of the 2,500 ppm of SO_2 in the tail gas.

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From the above estimate ozone oxidation efficiency would have to be about 30 or better (\$12/ton H_2SO_4 or less) for the process to be economical. This represents a control cost of \$.47.

TABLE 19

ESTIMATED OPERATING COST OF OZONE SYSTEM

<u>SO₂ Oxidized Mole O₃/Mole</u>	<u>Capital, Interest, Maintenance, etc., \$/Day</u>	<u>Power At \$0.01/KWhr and 3.75 KWhr/lb/O₃</u>	<u>Liquid Oxygen At \$10/Ton</u>	<u>Total</u>	<u>\$/Ton H₂SO₄ Recovered</u>
1	\$57.00	\$229.00	\$1,920.00	\$2,206.00	\$326.00
5	20.20	45.50	383.00	448.70	66.30
20	12.00	11.40	96.00	119.40	17.70
50	8.10	4.55	38.00	50.65	7.48
200	6.15	1.14	9.60	16.89	2.49

Chamber Acid Plant Emission Control

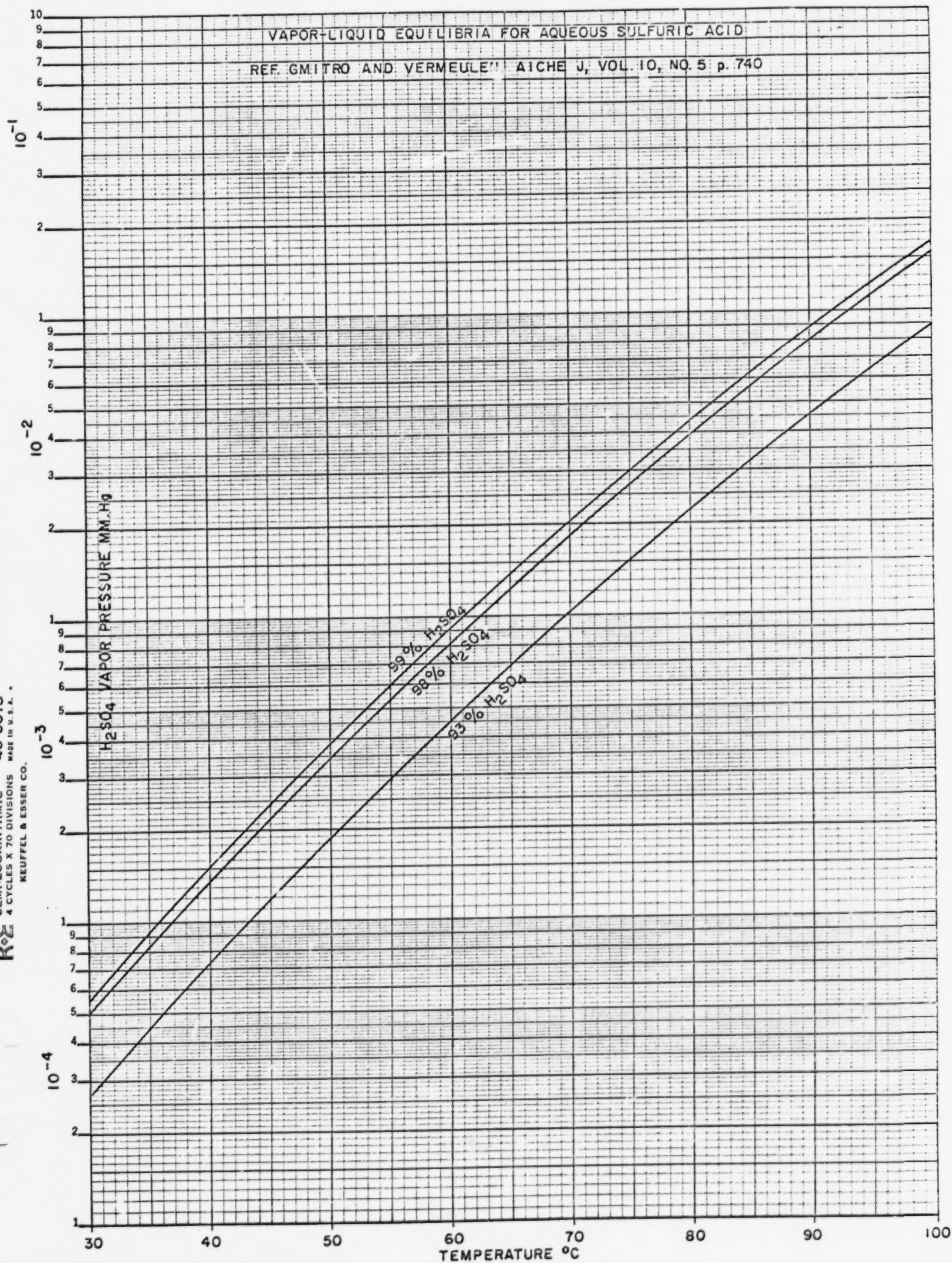
This recommendation is made to cover the one area of the sulfuric acid industry which cannot achieve effective control with any of the processes discussed in Part IV. Chamber plants are small, but could present local problems which would require a different approach than contact plants, since nitrogen oxides which are emitted are very difficult to absorb.

Should it be desirable to develop a control system suitable for chamber plants the following course is suggested.

A first step should be a review of the literature search which is Volume II of this report to determine the more promising absorbents or adsorbents for NO_x . A simple system would be desirable based on tests made with inexpensive media to determine which ones can efficiently entrain NO and NO_2 . The system can be an absorbing solution, a slurry, wet or dry solids. NO_x and SO_2 would probably require removal in two stages. A waste product which could be disposed of would be satisfactory, since quantities may be expected to be small.

A relatively inexpensive system for NO_x control might also find applications in other fields.

FIGURE 0



K&E SEMI-LOGARITHMIC 46 6013
4 CYCLES X 70 DIVISIONS
MADE IN U.S.A.
KEUFFEL & ESSER CO.

FIGURE D

1000 SERIES LOGARITHMIC
4 CYCLES X 70 DIVISIONS
MADE IN U.S.A.
KEUFFEL & ESSER CO.

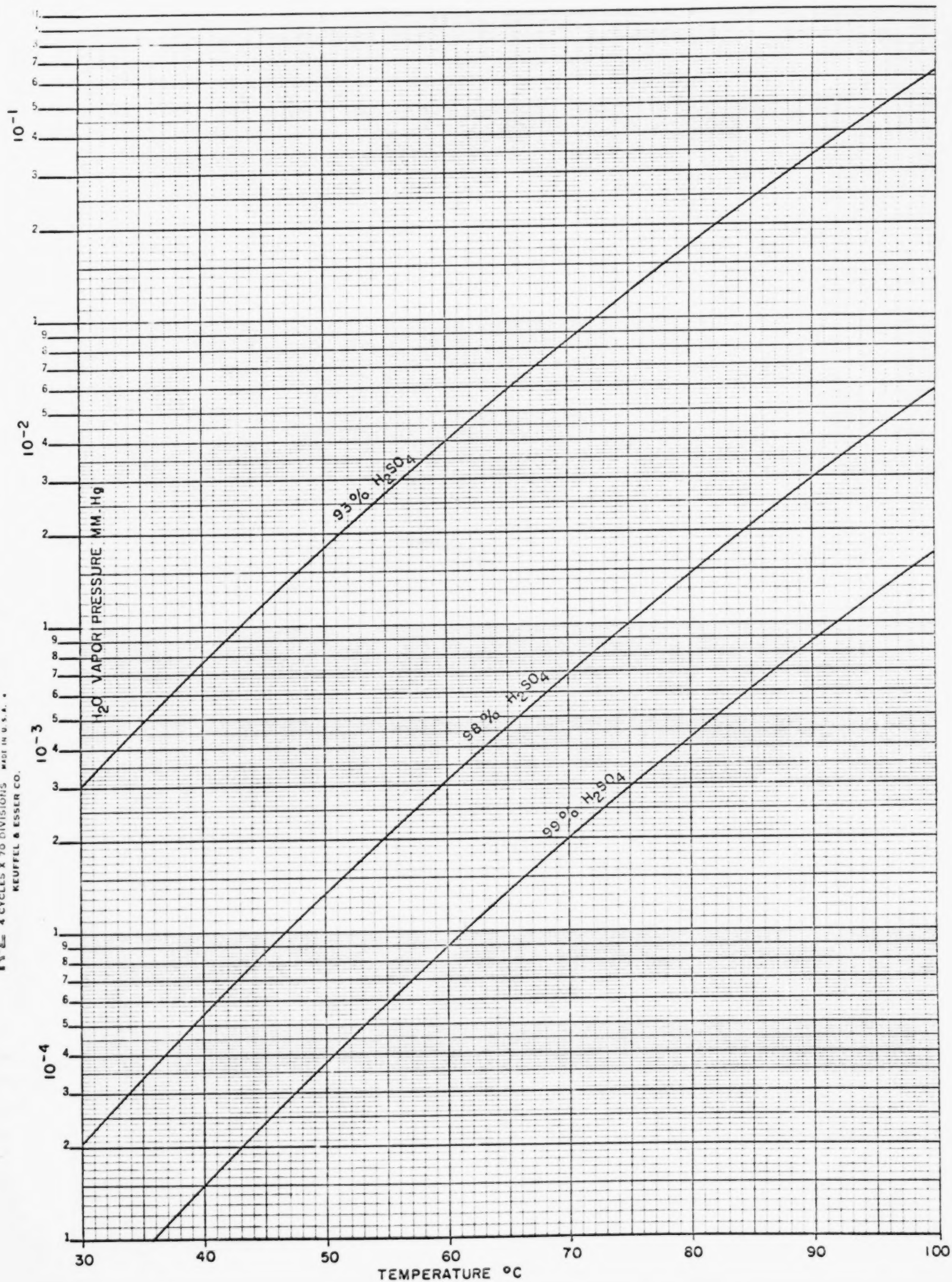
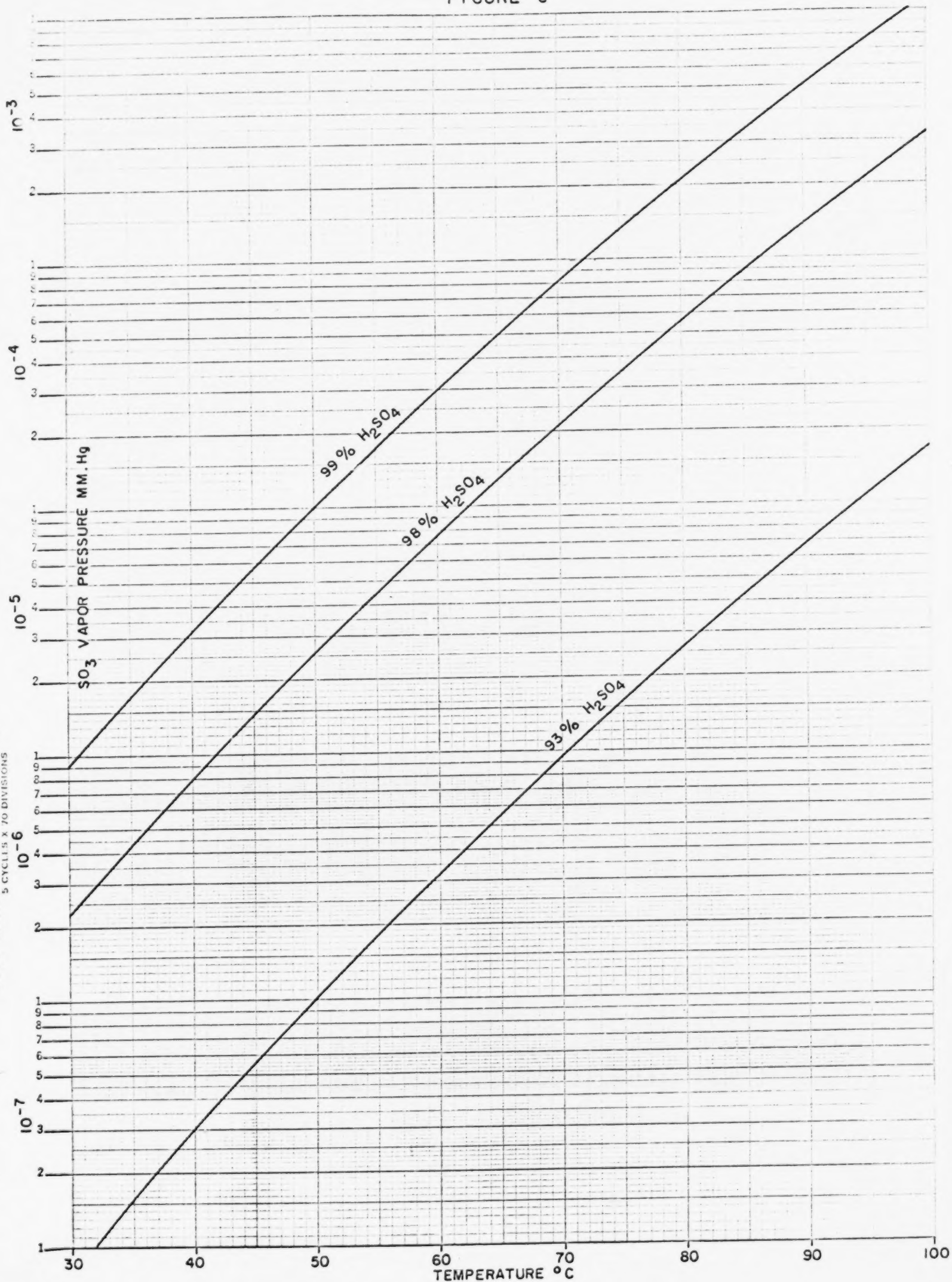
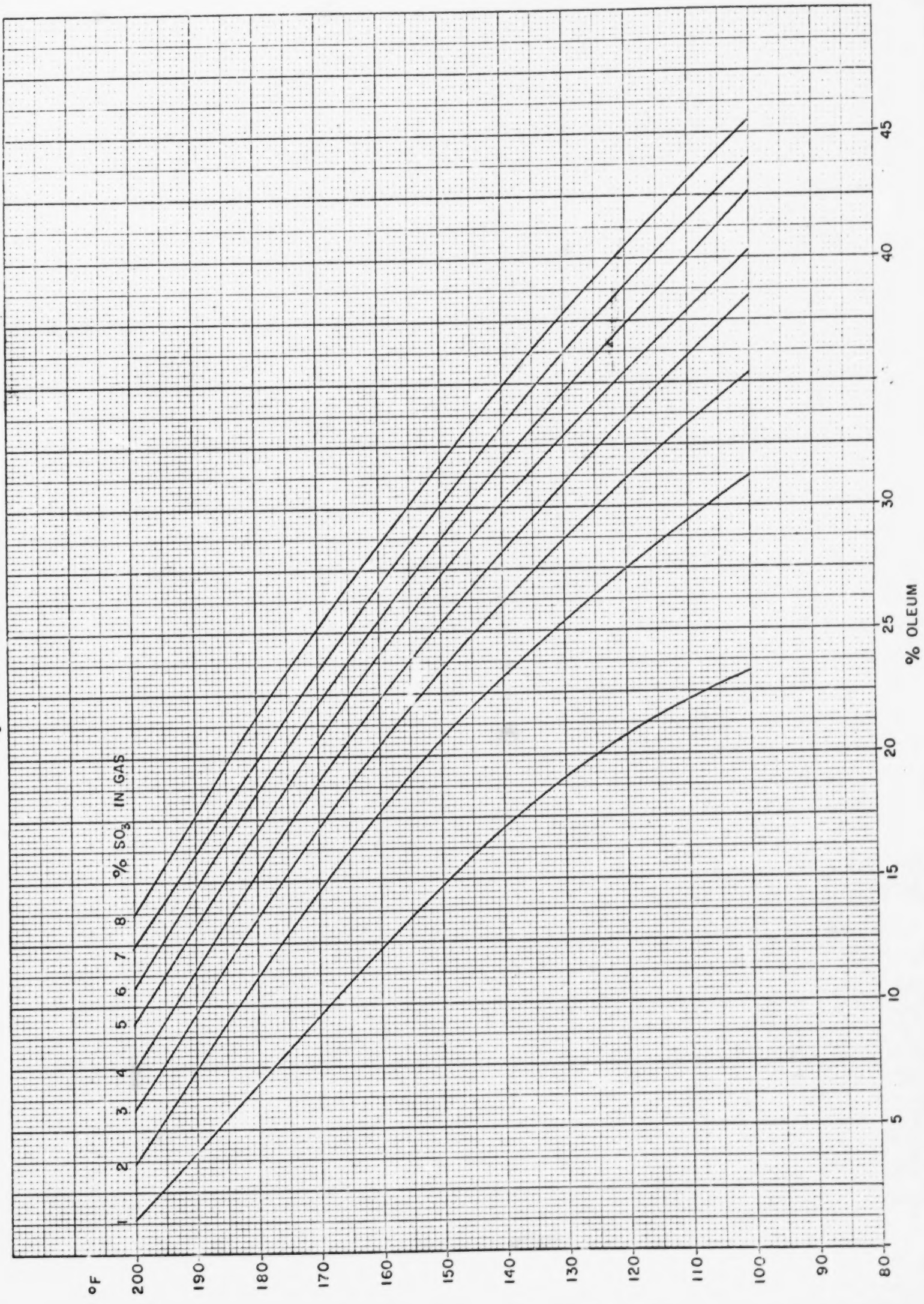


FIGURE C


 SEMI-LOGARITHMIC 358-91
 KEUFFEL & ESSER CO. MADE IN U.S.A.
 5 CYCLES X 70 DIVISIONS



SO₃ - OLEUM EQUILIBRIUM



SULFURIC ACID PRODUCTION COSTS

Plant Class	Process	Products	Conversion Rate	Estimated Production Cost - Dollars Per Short Ton of Acid (As 100% H ₂ SO ₄)					
				50 T/D	113 T/D	250 T/D	340 T/D	750 T/D	1,500 T/D
1.0	Chamber, Sulfur Burning	78% Acid	96.5%	\$18.50	\$13.74				
1.1	3-Stage Contact, Sulfur Burning	<99% Acid	95	17.85		\$11.17		\$ 9.84	
1.1	3-Stage Contact, Sulfur Burning	Acid + Oleum	95			11.26			
1.2	4-Stage Contact, Sulfur Burning	<99% Acid	96	22.30		13.43		11.25	\$10.38
1.2	4-Stage Contact, Sulfur Burning	Acid + Oleum	96			13.44			
1.2	4-Stage Contact, Sulfur Burning	<99% Acid	97.5	22.18		13.28		11.06	10.23
1.3	3-Stage Contact, Smelter Gas	<99% Acid	95.8	16.79		5.20		2.95	
1.4	4-Stage Contact, Smelter Gas	<99% Acid	96.8			8.80		5.01	3.74
1.4	4-Stage Contact, Smelter Gas	Acid + Oleum	96.8			9.12			
1.4	4-Stage Contact, Smelter Gas	<99% Acid	98.2					\$ 7.46	

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.1.1 - Dual Absorption (New Plant)

Description:

Similar to conventional contact plant up to conversion step. Absorption of SO_2 takes place after 2 or 3 conversion stages; SO_2 gas is reheated and returned to the converter for additional conversion and acid recovery in a second absorber. There are several variations depending upon conversion requirements and plant steam system.

Recovers:

SO_2 in the form of product H_2SO_4 for sale.

Status:

In commercial operation.

Licensors:

Bayer

Applications:

Reduced SO_2 emission from new sulfur burning contact plants.

Control Level Obtainable:

To 500 ppm for SO_2 ; no mist control

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Low

Reliability:

Same as modern contact plant.

Estimated Overall Worth:

Good.

Feasible. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.2.1 - Add-On Dual Absorption using Converter Heat.

Description:

Stack gas is heated utilizing a part of the heat of reaction from the converter. This gas is blown through a new secondary converter and absorber to produce additional acid product.

Recovers:

SO₂ in the form of product H₂SO₄ for sale.

Status:

Current technology, being offered commercially. . .

Licensors:

Chemico

Applications:

Reduce SO₂ emission from most sulfur burning contact plants.

Control Level Obtainable:

500 ppm for SO₂; no mist control.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Low

Reliability:

Good. Equal to existing plant

Estimated Overall Worth:

Good.

Feasible where space is available. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.2.2 - Add-On Dual Absorption using Furnace Heat

Description:

Stack gas is heated with hot furnace gas obtained by burning additional sulfur in the sulfur furnace, which bypasses the boiler system and first converter. The additional SO_2 + stack gas is converted to SO_3 in a new two stage secondary converter, and passed through a secondary absorber to provide additional acid product.

Recovers:

SO_2 in the form of product H_2SO_4 for sale.

Status:

Current technology being offered commercially.

Patents:

Applied for.

Licensors:

Chemico

Applications:

Reduce SO_2 emission from most sulfur burning contact plants to ≤ 500 ppm.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Low

Reliability:

Good - equal to existing plant.

Estimated Overall Worth:

Good.

Feasible where space is available. Additional production limited by furnace and blower capacity of existing plant.

Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.2.3 - Add-On Dual Absorption using Outside Heat Source

Description:

Stack gas is heated in a fired heater and blown through a new secondary converter and absorber to produce additional product acid.

Recovers:

SO₂ in the form of product H₂SO₄ for sale.

Status:

Current technology.

Applications:

Reduce SO₂ emission from wet gas contact plants.

Control Level Obtainable:

500 ppm for SO₂; no mist control.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Good - equal to existing plant.

Estimated Overall Worth:

Fair.

May be feasible for some wet gas plants.

Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.3.1 - Ultraviolet Oxidation of SO₂-

Description:

SO₂ gas is passed into a chamber irradiated with ultraviolet at 1,850Å. The SO₂ is oxidized to SO₃ and the latter is recovered in an additional 98% absorber producing acid.

Recovers:

SO₂ in the form of SO₃ for absorption to H₂SO₄.

Status:

Experimental

Applications:

Reduction of SO₂ emission for most contact plants.

Control Level Obtainable:

About 500 ppm for SO₂; no mist control.

Expected Relative Cost:

Capital Cost
Operating Cost

Average
High Power Cost

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Oxidation efficiency of ultraviolet has been reported to be poor.

Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.3.2 - Ozone injection to Catalyze Oxidation of Remaining SO₂-

Description:

Relatively small amounts of ozone are injected into the system between the economizer and the 98% tower. The ozone in the presence of SO₃ decomposes into atomic oxygen and an active O₂. This decomposition reaction produces a mild shock wave which causes SO₂ and O₂ in the gas to react to form SO₃. The ozone is generated separately from oxygen in an ozonator.

Recovers:

SO₂ in the form of SO₃ for absorption to H₂SO₄.

Status:

Requires testing.

Patents:

To be applied for.

Applications:

Reduce SO₂ emission from most contact plants.

Control Level Obtainable:

About 500 ppm for SO₂; no mist control.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown-The oxidative effect of ozone in an SO₃-SO₂ mixture has to be tested. This type of reaction has not been reported in the literature. A critical factor in this process is the oxidation efficiency of the ozone because the primary cost would be the capital and operating cost of the ozonator equipment.

Not presently feasible; may have potential.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.3.3 - Formation of Oxysulfuric Acid to Oxidize Remaining SO₂-

Description:

A portion of the SO₃ gas mixture is bled upstream of the 98% absorption tower. It is reacted with ozone generated with dried air to form peroxysulfuric acid. The oxy acid is passed counter current to the SO₃-SO₂ gas mixture in a separate section of the 98% tower. The SO₂ is converted to additional acid.

Recovers:

SO₂ in the form of H₂SO₄ for additional acid product.

Status:

Requires testing.

Applications:

SO₂ recovery for most contact plants.

Control Level Obtainable:

500 ppm for SO₂; no mist control.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-High

Reliability:

Acid plant reliability affected by reliability of additional equipment.

Estimated Overall Worth:

Unknown because of the following factors:

- (1) Ease of conversion of O₃ and H₂SO₄ to H₂SO₅
- (2) Absorption-oxidation of SO₂ in H₂SO₅ absorption section

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 1.3.4 - SO_2 - SO_3 Conversion Improvement by Catalyst Addition

Description:

Recently constructed contact H_2SO_4 plants can attain higher conversions either by restricting production rate or by additional catalyst.

Recovers:

SO_2 in the form of H_2SO_4 for sale.

Status:

Standard practice wherever applicable.

Applications:

For contact plants that already achieve over 96% conversion, to achieve 2,000 ppm; improvement for any contact plant.

Control Level Obtainable:

Will have to be determined individually. Improvement to 2,000 ppm can be expected.

Expected Relative Cost:

Capital Cost	Variable-Should be on low side.
Operating Cost	Very low

Reliability:

No change in reliability of existing plant.

Estimated Overall Worth:

Very good. Feasible for minor emission adjustments to most plants. Warrants further discussion.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.1 - Na_2CO_3 Absorption of SO_2 to Produce Na_2SO_3 -

Description:

SO_2 is absorbed in a concentrated sodium sulfite solution made alkaline with sodium carbonate. A bleed stream is indirectly heated with by-product steam from the acid plant in a scraped surface crystallizer. The crystal slurry is centrifuged and the crystals dried through indirect heat.

Recovers:

SO_2 in the form of Na_2SO_3 crystals for sale.

Status:

Pilot stage for SO_2 absorption-theoretical for crystallization.

Patents:

Chemico applications for SO_2 absorption and crystallization in venturi.

Applications:

SO_2 , or SO_2 , SO_3 and acid mist removal for most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	High-If sodium sulfite value is significantly less than soda ash.

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good, if sodium sulfite value is significantly greater than soda ash, sulfate formation can be controlled and by-product steam from acid plant can be utilized.

Feasible. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.2 - MgO Absorption of SO₂ to Produce MgSO₄-

Description:

SO₂ is absorbed in a magnesium sulfite-oxide slurry. An oxidation catalyst is added to the scrubbing liquid to facilitate oxidation of sulfite. The bleed stream containing the equivalent amount of SO₂ being absorbed as soluble sulfate and insoluble sulfite is fully oxidized at 130°F in an air sparging tank. The sulfate is then precipitated as the hydrated salt by evaporation.

Recovers:

MgSO₄ in the form of Epsom Salts for sale.

Status:

Absorption stage piloted; oxidation stage requires testing.

Patents:

Dow patent U.S. 1,801,661 (1931), for sulfite oxidation.

Applications:

SO₂, or SO₂, SO₃ and acid mist removal for most contact plants.

Control Level Obtainable:

About 100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good, if oxidation is efficient and there is a demand for the MgSO₄·7H₂O. Sulfite oxidation should be piloted.

If chemical processing is workable, the process would be feasible in specific areas.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2. 1. 3 - Lime Absorption of SO_2 to Produce Plaster of Paris

Description:

SO_2 is absorbed in a slurry containing hydrated lime. An oxidation catalyst is added. The bleed stream containing mainly sulfates and sulfites is sent to an air sparging tank to complete oxidation. The sulfate solids are centrifuged and dried to remove free water. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is then dehydrated to $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$.

Recovers:

SO_2 in the form of plaster of paris for sale.

Status:

Absorption in use, oxidation should be checked.

Patents:

Mitsubishi may have one.

Licensors:

Mitsubishi, but there can be many variations on this theme.

Applications:

SO_2 , or SO_2 , SO_3 and acid mist removal for most contact plants.

Control Level Obtainable:

100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good if Plaster of Paris market is available for quantities. Oxidation efficiency of sulfite is critical, as well as cost of oxidation catalyst.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.4 - Absorption with Ammonia-Oxidation of $(\text{NH}_4)_2\text{SO}_3$ to $(\text{NH}_4)_2\text{SO}_4$

Description:

SO_2 is absorbed in a solution containing a mixture of NH_4HSO_3 , $(\text{NH}_4)_2\text{SO}_3$ and $(\text{NH}_4)_2\text{SO}_4$. The equivalent amount of SO_2 absorbed is bled from the system as a mixture of bisulfite, sulfite and sulfate. The sulfite-bisulfite is air oxidized to sulfate and the latter is precipitated, centrifuged, washed and dried.

Recovers:

Ammonium Sulfate in the form of crystals for sale.

Status:

Piloted

Licensors:

Russian process, and others.

Applications:

Recover SO_2 or SO_2 , SO_3 and acid mist from most contact plants.

Control Level Obtainable:

100-200 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-High

Reliability:

Does not affect reliability of the acid plant.

Estimated Overall Worth:

Possible if there is a demand for ammonium sulfate.

Not promising in U.S.A.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.5 - SO_2 to Convert Phosphate Rock to Salable Fertilizer

Description:

SO_2 is absorbed in an $\text{NH}_4\text{HSO}_3 = (\text{NH}_4)_2\text{SO}_3 - (\text{NH}_4)_2\text{SO}_4$ solution. The sulfite-bisulfite is oxidized to sulfate and the sulfate precipitated. Dried sulfate is then heated to 300°C forming NH_3 for recycle and ammonium bisulfate. The acidic ammonium bisulfate is reacted with phosphate rock to form ammonium dihydrogen phosphate, ammonium sulfate and calcium sulfate.

Recovers:

SO_2 in the form of ammonium dihydrogen phosphate and ammonium sulfate for sale.

Status:

Experimental

Patents:

Very probable.

Licensors:

Kiyoura-T.I.T.

Applications:

SO_2 or SO_2 , SO_3 and mist removal for most contact plants.

Control Level Obtainable:

100-200 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair, ammonium dihydrogen phosphate (mono-ammonium phosphate) may be a more desirable fertilizer product than ammonium sulfate. Ammonium sulfate decomposition can be studied as well as market study for fertilizer products.

Complex - not presently promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.6 - The Production of Peroxydisulfuric Acid to Absorb and
Oxidize SO₂-

Description:

SO₂ is absorbed and oxidized in a scrubber with concentrated sulfuric acid solution containing persulfuric acids and hydrogen peroxide. A bleed stream of the concentrated H₂SO₄ is passed through an electrolytic cell to produce the oxy acid and H₂O₂. The H₂SO₄ is heated to remove oxygen before recycling to the acid plant and electrolytic cells.

Recovers:

Sulfuric acid in the form of 40-80% H₂SO₄ for sale.

Status:

Peroxide oxidation tried at bench scale.

Patents:

Simon-Carves Ltd. 930,584 Brit.

Applications:

SO₂ or SO₂, SO₃ and acid mist recovery for most contact plants.

Control Level Obtainable:

500 ppm or lower overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Many processing problems including oxidant efficiency and excess oxidant required for scrubbing liquid. Power costs are 0.3 mils per pound of acid. Cell costs will probably be high.

High capital cost.

Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.7 - Oxidation of SO₂ in Air-SO₂ Battery

Description:

The SO₂ gas is oxidized and hydrolyzed to H₂SO₄ in the anode compartment of an electrolytic cell. Air is passed into the cathode compartment where the oxygen is reduced. A concentrated H₂SO₄ product is recycled to the acid plant. Power generated by the cell is approximately 800 KWH/Ton of SO₂.

Recovers:

SO₂ in the form of sulfuric acid for recycle and sale --
D. C. power is generated.

Status:

Experimental work; "The Reaction of Sulfur Dioxide, Water and Oxygen in an Electrolytic Cell", W. F. Seyer et al, Transactions of the Electro Chemical Society, Vol. 91, 133-146 (1947).

Applications:

SO₂ recovery for most contact plants.

Control Level Obtainable:

Unknown

Expected Relative Cost:

Capital Cost	High
Operating Cost	High-Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Experimental.

Not presently feasible - theoretical concept.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.8 - Oxidation of SO₂ in Selenium Oxide Slurry

Description:

SO₂ is absorbed and oxidized in a slurry of selenious acid in 30% H₂SO₄. The SO₂ is oxidized to H₂SO₄ and the selenium reduced to the metal. The Se is regenerated by air oxidation.

Recovers:

SO₂ in the form of sulfuric acid for sale or recycle.

Status:

German and Belgian processes.

Patents:

German 1,204,770 (1963)

Licensors:

Badische Anilin- & Soda-Fabrik A.G.

Applications:

SO₂ or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

100-500 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor - Problem of contamination of H₂SO₄ product with selenium plus cost of selenium make-up at \$4.50/lb.

Not feasible - high cost of selenium.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.1.9 - SO_2 Absorption with Na_2CO_3 to Produce Na_2SO_4

Description:

SO_2 is absorbed in a sodium sulfite-sulfate solution made alkaline with Na_2CO_3 . An oxidation catalyst such as MnSO_4 or NaNO_2 is added to convert sulfite to sulfate. Oxidation is completed in an air sparging tank. The bleed stream is then evaporated precipitating anhydrous Na_2SO_4 . The sulfate is then centrifuged and dried.

Recovers:

Sodium Sulfate in the form of crystals for sale.

Status:

Absorption piloted; crystallization theoretical and requires piloting.

Applications:

SO_2 or SO_2 , SO_3 and acid mist removal from most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost
Operating Cost

Average
High-If sodium carbonate value is significantly greater than sodium sulfate.

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good, if there is a demand for sodium sulfate.

Technically feasible process but there is a greater demand for sodium sulfite. In addition, sodium sulfate has a lower market value than sodium sulfite.

Not as promising as 2.1.1.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.1 - Absorption and Recovery of SO_2 with Na_2SO_3 - NaHSO_3 Solution.

Description:

SO_2 is absorbed in two stages, with sulfite-bisulfite solutions. The bleed stream from the 1st stage is steam stripped releasing SO_2 . This gas is cooled to 100°F and dried in the 93% tower before recycle to the converter. Sulfates can be removed with lime, or the acid mist and SO_3 scrubbed out prior to the absorption and an oxidation inhibitor added to the absorbant solution.

Recovers:

SO_2 in the form of a concentrated gas for recycle to acid plant.

Status:

A considerable amount of work has been done.

Patents:

H. F. Johnstone, and many others.

Applications:

SO_2 or SO_2 , SO_3 acid mist recovery for most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High-Average (one stage)
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair; steam requirements may be excessive (12 lbs. steam/lb. SO_2) and sulfate formation would increase capital and operating cost.

Considered because steam is available at acid plant.

Feasible process, but utilities are higher than 2.2.8.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.2 - SO_2 Absorption with Na_2SO_3 - NaHSO_3 Solution; Recovery of SO_2 with ZnO . Sodium Sulfite-Bisulfite and Zinc Oxide.

Description:

SO_2 is absorbed in 2 stages in a sodium sulfite-bisulfite solution. ZnO is added to the bleed stream to react with the bisulfite to form insoluble zinc sulfite and sodium sulfite. The ZnSO_3 is calcined at 850°F to SO_2 and ZnO . Sodium sulfite is recycled to the absorbers. The ZnO is recycled and the SO_2 is cooled to 100°F and returned to the acid plant drying tower. Sulfates are removed with lime, or acid mist and SO_3 scrubbed prior to the absorption step and an oxidation inhibitor added to the absorbant solution.

Recovers:

SO_2 in the form of concentrated gas for recycle to acid plant.

Status:

Johnstone Process - Worked out thoroughly in laboratory.

Patents:

H. F. Johnstone - 2,161,056 (1937)

Applications:

SO_2 or SO_2 , SO_3 and acid mist removal from contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Depends upon ease of precipitation of zinc sulfite and losses of zinc. Would probably be less feasible than steam stripping of bisulfite-sulfite solution at acid plant sites since steam is available. Relatively high labor requirements.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.3 - Absorption of SO_2 with MnO_2 - $\text{Mg}(\text{OH})_2$ and Recovery by
Calcination (Grillo Process)

Description:

SO_2 is absorbed by a mixture of $\text{Mg}(\text{OH})_2$ - MnO_2 slurry. The sulfur salt product is MgSO_3 - MnSO_4 which is calcined with ground coal in a Herreshoff type furnace. The products are SO_2 , magnesium manganite and ash. The magnesium manganite is separated from the coal ash by flocculation reforming $\text{Mg}(\text{OH})_2$ and MnO_2 for absorption.

Recovers:

SO_2 in the form of concentrated gas for recycle.

Status:

Pilot plant - Oct. 1967, 12,000 CFM oil burner stack gas.

Patents:

British - 1,444,071

Licensors:

A.G. Fur Zinc Industrie

Applications:

SO_2 or SO_2 , SO_3 and acid mist recovery for most contact plants.

Control Level Obtainable:

100-500 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair. Reported fuel requirements for calcination are relatively low. Capital costs high since process includes 2 spray towers and Herreshoff type furnace, plus additional processing. Flocculation of alkali absorbent from coal ash requires testing. Not as promising as other processes.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.4 - Absorption of SO₂ with NaOH solution; Recovery of SO₂ and NaOH with Reducing Agent

Description:

SO₂ and SO₃ is absorbed in a concentrated solution of sodium sulfite made alkaline with sodium hydroxide. The bleed stream is heated to 1200-1400°C by the partial combustion of hydrocarbon vapors in a reducer reactor. Molten NaOH and SO₂ gas are formed. The SO₂ gas is cooled and recycled to the acid plant.

Recovers:

SO₂ in the form of SO₂ for recycle.

Status:

May have been piloted.

Patents:

Canadian - 817,327 7-8-69 Wilhelm Delters

Licensors:

Inventa A.G. Fur Forschung Und Patentverwertung,
Zurich, Switzerland

Applications:

SO₂ or SO₂, SO₃, and acid mist recovery from most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor

Not promising due to excessive fuel requirements. \$40/ton of sulfur, and incomplete conversion of sulfide intermediate to hydroxide. Fuel consumption can be somewhat reduced by precipitating crystals from the bleed stream.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.5 - Absorption of SO_2 with Na_2CO_3 and Reduction to Sulfur
with $\text{CO}+\text{H}_2$ Reform Gas

Description:

SO_2 is absorbed in a concentrated sodium sulfite solution made alkaline with soda ash. A bleed stream is cooled to precipitate hydrated sulfite. The sulfite is then heated to precipitate the anhydrous salt which is then centrifuged and dried. The sulfite is then reduced to sulfide with CO and H_2 and the sulfide reacted with CO_2 and steam to form soda ash and hydrogen sulfide. The H_2S is converted to elemental sulfur.

Recovers:

SO_2 in the form of elemental sulfur for recycle.

Status:

Extensive bench scale and pilot work done by Chemico.

Patents:

Applied for.

Applications:

SO_2 , or SO_2 , SO_3 and acid mist recovery from sulfur contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair; there would be reductions in capital and operating costs if sodium sulfite crystals produced at many acid plants are processed at a central plant. The central plant could also process crystals from other SO_2 sources as well. Few prospective users make feasibility unlikely for acid plants.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.6 - Magnesium Oxide Absorption of SO₂ With SO₂ Recovery

Description:

SO₂ is absorbed in a magnesium sulfite-oxide slurry. The bleed stream is centrifuged. The hydrated salt is dried and the anhydrous sulfite calcined to magnesium oxide and SO₂. The SO₂ gas is scrubbed and the gas cooled and most of the water condensed before recycle to the 93% tower.

Recovers:

SO₂ in the form of concentrated gas for recycle to acid plant.

Status:

Piloted, and full-sized systems proposed. A variation in commercial use in pulp industry.

Patents:

Several

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

Circa 100 ppm

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Good.

Feasible. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.7 - Absorption and Recovery of SO_2 with MgSO_3 - $\text{Mg}(\text{HSO}_3)_2$ -
Solution

Description:

SO_2 is absorbed in a magnesium sulfite-bisulfite solution. Magnesium oxide is added to the bleed stream precipitating magnesium sulfite. The MgSO_3 is then dried and calcined to MgO and SO_2 . A portion of the MgO produced is cycled to the scrubber to neutralize the remaining bisulfite. The SO_2 is cycled to the acid plant similar to the magnesium oxide system 2.2.6.

Recovers:

SO_2 in the form of concentrated SO_2 gas for recycle to acid plant.

Status:

Piloted, and full-sized systems proposed.

Patents:

Chemico

Applications:

SO_2 or SO_2 , SO_3 and acid mist recovery from most contact plants.

Control Level Obtainable:

<200 ppm overall.

Expected Relative Cost:

Capital Cost	High-Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good; however, magnesium oxide process 2.2.6 considered more promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.8 - Potassium Sulfite-Bisulfite

Description:

SO₂ is absorbed in a KHSO₃·K₂SO₃ solution. The bleed stream is cooled precipitating potassium pyrosulfite which is separated then redissolved and steam stripped to K₂SO₃, releasing SO₂ which is cooled to condense moisture then cycled to the acid plant. The sulfite formed is recycled to the scrubbers. Sulfates can be removed from the system with lime, or removed prior to absorption, plus using an oxidation inhibitor with the sulfite-bisulfite solution.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Commercial scale unit under construction.

Patents:

Many on this type of process.

Applications:

Most sulfur and non-sulfur contact plants for recovery of SO₂.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average

Reliability:

Operates independently.

Estimated Overall Worth:

Good - steam consumption 9 lbs/lb SO₂ for vacuum crystallization and steam stripping.

Feasible. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.9 - SO₂ Absorption with K₃PO₄ to Form K₂S₂O₅ and its Conversion to Sulfur

Description:

SO₂ is absorbed in 2 stages using K₃PO₄ as alkali makeup to form K₂SO₃ and KHSO₃. The bleed from the first stage with KHSO₃ as the predominant solute is cooled, precipitating K₂S₂O₅. The K₂S₂O₅ is heated to evolve 1/3 of the sulfur as SO₂. The remainder of the sulfur as K₂S₂O₅ and K₂SO₃ is reduced with reform gas to H₂S, then sulfur.

Recovers:

SO₂ in the form of sulfur for recycle.

Status:

Small scale testing has been done.

Patents:

TVA

Licensors:

TVA

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Does not affect reliability of the acid plant.

Estimated Overall Worth:

May have poor absorption efficiency due to build-up of phosphoric acid. Costly; pyrosulfite crystals should be processed at a central plant as suggested for process 2.2.5.

Not presently promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.10 - Absorption of SO₂ by K₂SO₃-KHSO₃; Recovery of SO₂ with Aldehyde Bisulfite

Description:

SO₂ is absorbed in a potassium sulfite-bisulfite solution. An organic such as an aldehyde is added to the bleed stream precipitating an aldehyde-bisulfite addition product which is then heated to release SO₂ and form a separated sulfite and aldehyde which are recycled. The SO₂ is cooled to 100°F and is then sent to the acid plant drying tower.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Theoretical

Patents:

None so far on this method.

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

<100 ppm overall may be possible.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown - precipitation of organic bisulfite and decomposition of same has to be proven.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.11 - Absorption with Ammonia - Recovery of SO₂ from Ammonia Bisulfite

Description:

SO₂ is absorbed in an ammonium sulfite-bisulfite solution. The bleed stream is steam stripped releasing a concentrated SO₂ gas which is cooled to condense most of the moisture before recycle to the acid plant.

Recovers:

SO₂ in the form of concentrated gas for recycle to acid plant.

Status:

Laboratory development.

Patents:

U.S. - 2,233,841 (1941) and many others.

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery for most contact plants.

Control Level Obtainable:

About 100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair - similar to the sodium and potassium sulfite and bisulfite processes, but absorbing solutions would be higher in bisulfite to prevent the release of NH₃ into the SO₂ free off gas. This, in turn, reduces absorption efficiency.

Not very promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.12 - Absorption of SO₂ with Ammonium Sulfite and Bisulfite;
Recovery of SO₂ with ZnO

Description:

SO₂ is absorbed in an ammonium sulfite-bisulfite solution. Ammonia is added equivalent to the SO₂ absorbed. Zinc Oxide is added to the bleed stream precipitating zinc sulfite and producing ammonium hydroxide. The solution is heated to evolve NH₃ for recycle. The ZnSO₃ precipitate is then calcined to release SO₂ and regenerate zinc oxide. The SO₂ is cooled to condense moisture before recycle.

Recovers:

SO₂ in the form of concentrated SO₂ gas for recycle.

Status:

Unknown

Patents:

Czech - 111,472 (7/15/64)

Licensors:

Unknown

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

About 100 ppm overall.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair, not quite as good as steam strip recovery. Higher capital and operating cost and dust problem. Zinc oxide losses would be a factor.

Not presently promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

2.2.13 - Absorption of SO₂ with Manganese Oxides with Recovery of SO₂-
From MnSO₄-

Description:

SO₂ is absorbed in a slurry of manganese oxides with the formation of soluble manganese sulfate which is bled from the system. The bleed solution is heated precipitating anhydrous MnSO₄ which is separated by centrifuging. It is then calcined at 1,000°C releasing SO₂ and forming manganese oxides which are recycled. The SO₂ is then water-cooled to 100°F and then cycled to the acid plant.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

TVA-Piloted using counter-current absorption tower.

Patents:

U.S. - 2,984,545 (1961) (TVA)

Licensors:

TVA

Applications:

SO₂ or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

100-500 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor - Problems in regeneration of manganese oxides absorbent were encountered.

Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.14 - SO₂ Absorption in and Recovery From Methylammonium Sulfite-Bisulfite Solution

Description:

SO₂ is absorbed in methylammonium sulfite-bisulfite in two stages. A bleed stream containing the equivalent methylammonium bisulfite is steam stripped producing methylammonium sulfite and releasing SO₂. The former is returned to the scrubber and the SO₂ cooled to about 100°F to condense most of the H₂O before cycling to the acid plant. An oxidation inhibitor is added to the absorbing solution to reduce sulfate formation. Acid mist and SO₃ are scrubbed out prior to absorption.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Johnstone test data. Should be piloted.

Patents:

Possible Johnstone Patent circa 1940

Applications:

SO₂ or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

As low as 100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good. Steam requirements for desorption are a little high (18 lbs/lb. SO₂). Methylamine vapor pressure in methylammonium sulfite-bisulfite is negligible at absorption temperatures.

Feasible. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.15 - SO₂ Absorption in and Recovery From a Xylidine-Water Mixture (Sulphidine Process)

Description:

SO₂ is absorbed in a xylidine-water mixture. The xylidine sulfite is water soluble and is steam stripped releasing SO₂ and returning xylidine to the scrubber. The SO₂ is cooled then cycled to the acid plant. Some of the xylidine which is toxic can be vaporized into the flue. An additional absorption stage is required.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Process developed in Germany.

Patents:

Probably German patents.

Licensors:

Lurgi

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

100-500 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor; second scrubbing stage required using organic alkali and xylidine sulfate formation requiring Na₂CO₃ or Na₂SO₃ for regeneration.

Not promising because of volatility, toxicity and sulfate removal problems.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.16 - Sodium-Barium Salt System for Absorption of SO₂ and its Recovery As Sulfur

Description:

SO₂ is absorbed in a solution of NaSO₃ kept at the neutral point with Na₂CO₃. Barium sulfide is added to the Na₂SO₃ precipitating BaSO₃ and producing Na₂S. The BaSO₃ is reduced to BaS which is recycled. The Na₂S is converted to alkali (which is also recycled) and H₂S which is converted to elemental sulfur.

Recovers:

SO₂ in the form of elemental sulfur for recycle to plant.

Status:

Laboratory work at Chemico.

Patents:

To be applied for, and 1938 patent.

Applications:

SO₂ removal from most sulfur burning contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High-Average
Operating Cost	High-Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good if barium sulfite crystals are reduced to sulfide at central process plant to reduce costs. Not promising for most acid plants.

Similar to Na₂CO₃-S⁰ process 2.2.5.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.17 - Sodium-Barium Salt System for Absorption and Recovery of SO₂-

Description:

SO₂ is absorbed in a solution made alkaline with NaOH. The bleed stream containing a Na₂SO₃ solution is reacted with barium oxide precipitating barium sulfite and producing NaOH with the latter recycled to the scrubber. The barium sulfite is reduced to sulfide and the latter is then roasted to SO₂ and BaO. The SO₂ is cleaned and then cooled to condense moisture before recycle.

Recovers:

SO₂ in the form of concentrated gas for recycle to acid plant.

Status:

Laboratory work at Chemico on barium salt precipitation.

Applications:

SO₂ or SO₂, SO₃ and mist recovery from most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor. Sulfite has to be reduced in order to release the SO₂.

Not promising.

Additional processing required in comparison to other processes involving the calcination of a salt to release SO₂.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.18 - Absorption of SO₂ with Barium Hydroxide and its Recovery
from BaSO₃-BaSO₄-

Description:

SO₂ is absorbed in a solution made alkaline with barium hydroxide forming insoluble barium sulfite and sulfate. This material is bled from the scrubber, settled out and centrifuged. It is then reduced and roasted to release the SO₂.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Laboratory work at Chemico on barium salt precipitation.

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor, sulfite must be reduced in order to release SO₂.

Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.19 - Absorption of SO_2 in $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and H_2SO_4 liquid,
and its recovery from FeSO_4

Description:

SO_2 is absorbed and oxidized in a scrubbing liquid containing FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and H_2SO_4 . The SO_2 is oxidized to H_2SO_4 and the $\text{Fe}_2(\text{SO}_4)_3$ reduced to FeSO_4 . The FeSO_4 is calcined to SO_2 , SO_3 and Fe_2O_3 . The gas is cooled, removing the SO_3 as H_2SO_4 , and the SO_2 is cycled to the acid plant. The Fe_2O_3 is reacted with a bleed stream containing dilute H_2SO_4 and iron salts at elevated temperatures of about 300°F to reduce acidity level.

Recovers:

SO_2 in the form of SO_2 and SO_3 gas for recycle.

Status:

Idea

Patents:

None

Applications:

SO_2 , or SO_2 , SO_3 and acid mist recovery from most contact plants.

Control Level Obtainable:

500 ppm, possibly lower, overall may be possible

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown; absorption efficiency of SO_2 must be determined as well as dissolution of Fe_2O_3 in dilute H_2SO_4 at elevated temperatures.

Not presently promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.20 - Liquid Phase Oxidation of SO₂ with Ozone

Description:

Ozone is mixed with the exiting gases and sparged into a sulfuric acid solution. The SO₂ is oxidized to H₂SO₄ and the acid produced is cycled to the 93% tower.

Recovers:

SO₂ in the form of H₂SO₄ for recycle.

Status:

Experimental

Patents:

Many

Applications:

Most sulfur and non-sulfur contact plants for reduction of SO₂ emission.

Control Level Obtainable:

100-500 ppm SO₂ may be possible; no mist control.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Does not affect operation of acid plant.

Estimated Overall Worth:

Many unknown factors, including capital cost, oxidation efficiency (which must be well over 100%), the consequences of dissolved O₃ in H₂SO₄ and pressure drop in oxidation system. Pilot testing would be required.

Not presently feasible.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.21 - Activated Charcoal Slurry Absorption and Recovery of SO₂

Description:

SO₂ is absorbed in a slurry of absorbant carbon. The bleed stream containing equivalent SO₂ is centrifuged and the charcoal mass is heated to release adsorbed SO₂ and regenerate the charcoal.

Recovers:

SO₂ in the form of concentrated gas for recycle to acid plant.

Status:

Absorption piloted, regeneration unknown.

Patents:

Japan - 174,880 (1948)

Licensors:

Toa Gosei K.K.

Applications:

SO₂ recovery for most contact plants. Separate mist control advisable.

Control Level Obtainable:

100 to 500 ppm for SO₂.

Expected Relative Cost:

Capital Cost	Low-Average
Operating Cost	Average-High

Reliability:

Does not affect efficiency of acid plant.

Estimated Overall Worth:

Processing problems - active life of charcoal and its absorptive capacity; could be piloted.

Does not look too promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.22 - Absorption and Oxidation of SO₂ in Charcoal Beds
(Sulfacid Process)

Description:

SO₂ removed from various industrial waste gases. SO₂ converted to H₂SO₄ by wet catalysis. Product acid is 10+^o% H₂SO₄.

Recovers:

SO₂ in the form of H₂SO₄ for sale, reuse as scrubbing liquor concentration, or possible recycle to acid plant.

Status:

In use.

Licensors:

Lurgi Gesellschaft Fur Chemie und Huttenwesen mbH

Applications:

SO₂, SO₃ and acid mist recovery from most contact plants; most economical when applied to plants with low SO₂ emission level.

Control Level Obtainable:

<500 ppm

Expected Relative Cost:

Capital Cost	Installed Cost \$225,000 in Europe for 400 STD H ₂ SO ₄ Plant @ 1800 ppm emission
Operating Cost	Low

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Not the most feasible unless there is a proper water balance since a 10% acid is produced.

Economical applications may be limited in U.S.

Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.23 - Adsorption and Recovery of SO₂ with Activated Char
(Reinluft Process)

Description:

SO₂ is absorbed and oxidized to H₂SO₄ on activated char. The char is heated to 700° F reducing the H₂SO₄ to SO₂. A bleed stream containing hot SO₂ and CO₂ gases is cycled to the acid plant.

Recovers:

SO₂ in the form of concentrated gas for recycle to acid plant.

Status:

Large pilot unit.

Patents:

Yes

Applications:

SO₂, SO₃ and acid mist removal from most contact plants.

Control Level Obtainable:

100-500 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor - pilot units tested had operating difficulties.

Not feasible because of the operating difficulties and relatively large amount of char consumed as the reducing agent.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.24 - Adsorption of SO₂ with Dry Hydrated Lime with SO₂-
Recovery by Calcination

Description:

SO₂ is absorbed in a bed of dry hydrated lime. The spent sulfite and sulfate is calcined to lime which is then hydrated and recycled to the adsorber. The SO₂ is scrubbed and cooled and cycled to the acid plant. Carbon is added to the calciner for reduction of CaSO₄.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Idea

Applications:

SO₂ and mist removal from most contact plants.

Control Level Obtainable:

100-500 ppm overall may be possible.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown

Not presently promising. Requires extensive piloting to determine feasibility.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.25 - Adsorption and Recovery of SO₂ with Silica-Alumina Alkali

Description:

The off-gases from the plant are heated to 600-800^oF and passed over a fluidized silica alumina bed containing copper, chromium and barium. The adsorbant is regenerated at 675-825^oF using H₂, CO or CH₄. Sulfur is released as S^o, SO₂ and H₂S. The H₂S and S^o are burned and all the SO₂ is recycled.

Recovers:

SO₂ in the form of SO₂ for recycle.

Status:

Tested

Patents:

French - 1,448,396

Licensors:

Shell Internationale Research Maatschappij N. V.

Applications:

SO₂, SO₃ and mist recovery from H₂S and sludge burning plants.

Control Level Obtainable:

Probably to 100 ppm and lower, overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor - reducing agent is required plus adsorption at 600-800^oF. In addition, there might be high attrition of the adsorbant.

Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.26 - Adsorption and Recovery of SO₂ with Alkalized Alumina

Description:

SO₂ is adsorbed by Na₂O-Al₂O₃ pellets in a dry contactor forming Na₂SO₄-Al₂O₃. The pellet stream is bled into a reactor where reform gas reduces the sulfate to the oxide and releases H₂S which is recycled to the acid plant. The regenerated Na₂O-Al₂O₃ pellets are recycled to the dry contactor.

Recovers:

SO₂ in the form of H₂S for recycle.

Status:

Piloted by Bureau of Mines.

Patents:

Many

Licensors:

CEGB-England

Applications:

SO₂ recovery from most H₂S and sludge burning contact plants.

Control Level Obtainable:

About 100 ppm

Expected Relative Cost:

Capital Cost

Average-High

Operating Cost

High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Poor - excessive losses of alkalized alumina absorbant has made the process impractical.

Not feasible.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.27 - Adsorption of SO₂ with Dry Magnesia and Recovery from
MgSO₃-MgSO₄-

Description:

SO₂ is chemically adsorbed by a mixture of dry MgO-MgSO₃-MgSO₄ co-current in an adsorption tower. The exiting gas-solid mixture is separated. The MgO-MgSO₃-MgSO₄ is sent to a calciner where SO₂ is released and the MgO is recycled. SO₂ is cleaned, cooled and cycled to the acid plant.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

Process Piloted

Patents:

Applied for.

Licensors:

Showa Hatsuden, subsidiary of Showa Denko, K.K.

Applications:

SO₂ recovery from most contact plants.

Control Level Obtainable:

500 ppm SO₂ only.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown - adsorption stage would have to be piloted with the goal of 95% removal of SO₂. Dry adsorption type process is favorable for acid plant control since there is no moisture in the incoming gases.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.28 - Absorption with Basic Aluminum Sulfate Solution,
Regeneration with Heat to Release SO₂-
(Hardman Holden)

Description:

Sulfuric acid tail gas is scrubbed with a basic aluminum sulfate solution. SO₂ is recovered by steam stripping and recycled to the drying tower. SO₃ and acid mist must be removed before scrubbing.

Recovers:

SO₂ in the form of concentrated gas for recycle.

Status:

In commercial operation (Europe), for SO₂ production from sulfur.

Patents:

Many; U.S., British, German, Australian

Licensors:

Hardman Holden Ltd.

Applications:

SO₂ recovery from any contact acid plant.

Control Level Obtainable:

500 ppm or lower for SO₂ and mist.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good - Feasible, but SO₃ and acid mist must be removed prior to scrubbing to minimize sulfate formation.

Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.29 - Resin Adsorption of SO₂-

Description:

SO₂ is adsorbed by an ion-exchange resin. The resin is regenerated with hot air. Acid mist removed first by decomposition with heat to H₂O and SO₃, and SO₃ is adsorbed by separate adsorbent.

Recovers:

SO₂ in the form of SO₂ for recycle to the acid plant; removes SO₃ and acid mist.

Status:

Laboratory development.

Patents:

U. S. patent pending for resin.

Licensors:

Rohm & Haas (resin)

Applications:

SO₂ recovery and acid mist removal from any contact acid plant.

Control Level Obtainable:

200 ppm or lower depending on regeneration cycle.

Expected Relative Cost:

Capital Cost	Medium
Operating Cost	Low

Reliability:

High, independent operation does not affect acid plant reliability.

Estimated Overall Worth:

Good - further development required for SO₃ removal step.
Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.2.30 - Adsorption of SO₂ with a Molecular Sieve

Description:

SO₂ is adsorbed in a highly acid resistant synthetic variety of a mineral molecular sieve characterized with high pore properties. The molecular sieve is regenerated with hot gas at temperatures as low as 200°C.

Recovers:

SO₂ in the form of dilute gas.

Status:

Laboratory work has been done.

Patents:

Norton Company

Applications:

SO₂ removal from most contact plants.

Control Level Obtainable:

Unknown.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Low

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 4.3.1 - Absorption of SO₂ with Acetic Acid Solubilized Limestone Slurry

Description:

SO₂ is absorbed in a limestone slurry containing a small amount of acetic acid. The bleed stream containing mainly sulfites and sulfates is sent to a clarifier. The underflow is centrifuged and solids sent to waste disposal. The supernatant liquid containing acetic acid is recycled.

Recovers:

SO₂ in the form of calcium magnesium sulfites and sulfates for disposal.

Status:

Bench scale tests for absorption of SO₂ and solubility of limestone in acetic acid.

Patents:

Chemico patent applied for.

Applications:

SO₂ or SO₂, SO₃ and acid mist removal for most contact plants.

Control Level Obtainable:

200-300 ppm overall.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Average

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good, if SO₂ emissions are relatively low, inexpensive limestone is available and solids can easily be disposed of. Limestone solubility and acetic acid volatility requires evaluation in a pilot scrubber. The acetic acid reduces the variability of limestones with regard to their alkali consumption efficiencies and SO₂ absorption efficiencies. Acetic acid volatility would be minimal since the absorbing slurries would be at about 75°F.

Too many unknowns for further evaluation here.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.3.2 - Absorption of SO₂ in Limestone Slurry

Description:

SO₂ is absorbed in a limestone slurry. The bleed stream containing mainly sulfites and sulfates is sent to a clarifier. The underflow is centrifuged and the solids sent to solid waste disposal. The supernatant liquids are recycled.

Recovers:

SO₂ in the form of calcium and magnesium sulfite and sulfate for disposal.

Status:

Has been piloted for utility applications.

Patents:

Many

Applications:

SO₂, SO₃ and acid mist removal from most contact plants.

Control Level Obtainable:

500 ppm or lower overall.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Good if regulations are not too strict, inexpensive limestone is available, and the solids can be easily disposed of.

SO₂ absorption efficiency may not be as high as desired.

Not as promising as 2.3.3.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.3.3 - Lime Absorption of SO₂

Description:

SO₂ is absorbed in a slurry containing hydrated lime. The bleed stream which contains mainly sulfites and sulfates is sent to a clarifier. The underflow is centrifuged and the solids sent to waste disposal. The supernatant liquid is recycled.

Recovers:

Calcium sulfites and sulfates in the form of solids for disposal.

Status:

In use on utility boilers in similar process.

Patents:

Many

Applications:

Most sulfur and non-sulfur contact plants.

Control Level Obtainable:

Circa 100 ppm possibly lower.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Average-High

Reliability:

Operates independently.

Estimated Overall Worth:

Good if SO₂ emissions are relatively low and solid waste disposal facilities are available.

Feasible. Shows enough promise to warrant future evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.1 - Absorption and Recovery of SO_2 , and Production of Na_2SO_4 -

Description:

SO_2 is absorbed in a sodium sulfite solution with the entering Na_2CO_3 neutralizing the bisulfite formed. Sulfuric acid is added to the bleed stream releasing SO_2 and forming sodium sulfate. The SO_2 is highly concentrated and is sent to the 93% tower to remove any moisture before recycle to the converter. The Na_2SO_4 solution is evaporated precipitating anhydrous crystals.

Recovers:

SO_2 in the form of concentrated SO_2 gas and salt cake for recycle and sale respectively.

Status:

Absorption piloted, crystallization industrial process.

Patents:

Many

Applications:

SO_2 , or SO_2 , SO_3 and acid mist removal from most contact plants.

Control Level Obtainable:

100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Technically good but poor economics. Similar to sodium sulfate process 2.1.9, plus the cycling of SO_2 .

Not as promising as sodium sulfate process 2.1.9 because H_2SO_4 is consumed to produce Na_2SO_4 .

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.2 - Absorption and Oxidation of SO₂ Producing MgSO₄ From MgO

Description:

SO₂ is absorbed in two stages. In the first a dilute H₂SO₄ solution containing MnSO₄ catalyst absorbs and oxidizes 1/2 the sulfur values entering the system. The remaining SO₂ gas is absorbed in a magnesium sulfite-oxide slurry. The acid in the first stage is reacted with the MgSO₃ from the second forming MgSO₄ and SO₂. The MgSO₄ is crystallized and the SO₂ recycled.

Recovers:

SO₂ in the form of SO₂ gas for recycle and MgSO₄ · 7H₂O for sale.

Status:

Idea

Patents:

None

Applications:

SO₂, or SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-Low

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair, 1/2 SO₂ returned to plant. Dilute impure acid is utilized to form a fairly pure magnesium sulfate which can be sold. Only 50% absorption of SO₂ is required in the first stage where absorption is difficult. At an acid plant there are no phenols to inhibit oxidation as with coal-fired boilers. Dilute MgSO₄ solution would be formed requiring considerable evaporation for crystallization since the acid formed is dilute.

Magnesium sulfate has a limited market (Process 2.1.2). Not promising.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.3 - Fulham Simon-Carves; Production of Sulfur and $(\text{NH}_4)_2\text{SO}_4$ from $(\text{NH}_4)_2\text{SO}_3$ - NH_4HSO_3 Solution

Description:

SO_2 is absorbed in an ammonium sulfite-bisulfite solution. A relatively small amount of sulfuric acid is added to the bleed stream and the material autoclaved. Ammonium sulfate and elemental sulfur are produced at a weight ratio of 13 to 1.

Recovers:

SO_2 in the form of sulfur and $(\text{NH}_4)_2\text{SO}_4$ for recycle and sale, respectively.

Status:

Pilot stage.

Patents:

British 525,883 (1940)

Licensors:

Fulham Simon-Carves Ltd.

Applications:

SO_2 or SO_2 , SO_3 and acid mist recovery from most sulfur burning contact plants.

Control Level Obtainable:

100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Fair - There is little demand for ammonium sulfate which is the principal product. A relatively small amount of SO_2 is recycled.

Not as promising as other systems.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.4 - Absorption of and Recovery of SO_2 Using $(\text{NH}_4)_2\text{SO}_3$ -
 NH_4HSO_3 and H_2SO_4

Description:

SO_2 is absorbed in an ammonium sulfite-bisulfite solution. Sulfuric acid is added to the bleed stream releasing SO_2 and forming ammonium sulfate. The SO_2 is highly concentrated and is sent to the 93% tower to remove any moisture before recycle to the converter. The ammonium sulfate is crystallized from solution.

Recovers:

SO_2 in the form of concentrated gas for recycle and $(\text{NH}_4)_2\text{SO}_4$ for sale.

Status:

In Use

Patents:

Cominco

Licensors:

Cominco

Applications:

Most sulfur and non-sulfur contact plants.

Control Level Obtainable:

Circa 100 ppm

Expected Relative Cost:

Capital Cost	Average
Operating Cost	High

Reliability:

Operates independently.

Estimated Overall Worth:

Fair; high operating costs, H_2SO_4 and NH_3 raw materials, ammonium sulfate product.

Not promising except under special circumstances where it may be quite attractive.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.5 - Ammonium Sulfite-Bisulfite Absorption with SO₂ Recovery
and NH₄NO₃ Production

Description:

SO₂ is absorbed in two stages in solutions of ammonium sulfite-bisulfite. Nitric acid is added to the ammonium sulfite-bisulfite bleed stream releasing SO₂ for recycle and forming ammonium nitrate. The ammonium nitrate in solution form is concentrated for sale. Ammonium sulfate formed is removed with the nitrate product.

Recovers:

Concentrated SO₂ for recycle and ammonium nitrate for sale.

Status:

In commercial operation in Europe.

Licensors:

SCHIZ (Czechoslovakia)

Applications:

SO₂, SO₃ and acid mist recovery from most contact plants.

Control Level Obtainable:

About 100 ppm overall.

Expected Relative Cost:

Capital Cost	High
Operating Cost	High

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Good in locations where there is demand for NH₄NO₃ solution.
Feasible. Shows enough potential to warrant future evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 2.4.6 - Sulfuric Acid-Lime 2 Stage Absorption to Recover SO₂ and Produce Plaster of Paris

Description:

SO₂ is absorbed in 2 stages. In the first, a 10% H₂SO₄ solution containing MnSO₄ catalyst absorbs and oxidizes half the sulfur values entering the system. The remaining sulfur value is absorbed in the second stage with lime. The acid is then reacted with the CaSO₃ product to form SO₂ which is recycled, and CaSO₄-2H₂O which is calcined to CaSO₄-1/2H₂O.

Recovers:

Concentrated SO₂ for recycle and plaster of paris for sale.

Status:

Idea

Patents:

Russian #50446 (1937)

Applications:

SO₂, SO₃ and acid mist recovery for most contact plants.

Control Level Obtainable:

<100 ppm overall.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-High

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Good. Shows enough potential to warrant further evaluation.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.1.1 - Dual Pad Mist Separator

Description:

Acid mist impinges on filaments of horizontal mesh pads located in top of the absorption tower to form large droplets which are returned to the tower by gravity.

Recovers:

H_2SO_4 mist in the form of H_2SO_4 for sale as product.

Status:

Many types in commercial operation.

Patents:

Many.

Applications:

Recovery of acid mist particles >3 microns from most acid plants not producing oleum.

*Control Level Obtainable:

Reduce acid mist to 2 mg/ACF.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Low

Reliability:

High - Does not affect acid plant reliability.

Estimated Overall Worth:

Good - Feasible within its range of capability. Low gas velocities required.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.1.2 - Tubular Type Mist Separator

Description:

Tail gas from the absorption tower passes through glass fiber packed vertical tubular elements. Recovered acid mist flows down the inside of the elements and is returned to the tower as liquid.

Recovers:

H_2SO_4 mist in the form of H_2SO_4 for sale.

Status:

In commercial operation.

Patents:

Several.

Licensors:

Monsanto (Brinks High Efficiency)

Applications:

Recovery of acid mist for most acid plants.

Control Level Obtainable:

Reduce acid mist emission to ≤ 0.1 Mg/SCF.

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Low

Reliability:

High - Does not effect plant efficiency.

Estimated Overall Worth:

Good. Feasible.

Can be accommodated within the absorber in new plants.
Existing plants require separate unit.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.1.3 - Panel Type Mist Separator

Description:

Tail gas from the absorption tower passes through vertical fiber panels into a chamber. Tail gas is discharged upward and collected mist as liquid is collected in a drain line and returned to the absorber.

Recovers:

Acid mist in the form of H_2SO_4 for sale.

Status:

In commercial operation.

Patents:

Several.

Licensors:

Monsanto (Brinks High Velocity)

Applications:

Acid mist recovery for most acid plants.

Control Level Obtainable:

Reduce acid mist emission to <0.5 Mg/SCF.

Expected Relative Cost:

Capital Cost	Low - Average
Operating Cost	Low

Reliability:

High - Does not affect acid plant reliability.

Estimated Overall Worth:

Good - Feasible.

Can be accommodated within the absorber in new plants; existing plants require a separate unit.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.2.1 - Electrostatic Precipitation

Description:

Tail gas is passed through a chamber with electrostatic elements. Mist particles collect on the elements and fall as liquid to the bottom of the chamber and are returned to the acid plant.

Recovers:

H_2SO_4 mist in the form of H_2SO_4 for sale.

Status:

In commercial operation.

Patents:

Many.

Applications:

Acid mist recovery for most acid plants.

Control Level Obtainable:

To 99% mist removal. Near 100% for <3 micron mist.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average-High

Reliability:

Good - Does not affect reliability of acid plant.

Estimated Overall Worth:

Good- Feasible

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.3.1 - Mist Removal With Venturi Scrubber

Description:

H_2SO_4 mist is entrained in a venturi scrubber operating at high pressure drop (30" to 40" H_2O). The scrubbing liquid may be water or H_2SO_4 . The bleed stream can be neutralized with alkali and the salt disposed of if applied to a contact plant. This is not necessary with a concentrator.

Recovers:

Acid mist in the form of $CaSO_4$ for disposal, or weak acid for concentration.

Status:

Venturi scrubbers are in commercial operation on concentrators.

Patents:

Many

Applications:

All acid plants except oleum for acid mist control.

Control Level Obtainable:

$< 3 \text{ Mg } H_2SO_4 / SCF$

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	Average

Reliability:

High. Does not affect reliability of acid plant.

Estimated Overall Worth:

Good for elimination of most acid mist problems, but more costly than 3.1.1 for equal control on a contact plant.

Feasible for concentrators (classifications 1.5 and 2.5).

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 3.4.1 - Absorption and Neutralization of Acid Mist and SO₃ with Lime

Description:

Lime as fine dust is injected into the tail gas upstream of a venturi scrubber. The lime reacts with the acid mist and SO₃ vapor to form CaSO₄ which is removed in the venturi. The scrubbing medium is a CaSO₄ slurry in H₂SO₄.

Recovers:

H₂SO₄ mist and SO₃ in the form of CaSO₄ for disposal.

Status:

Some laboratory work has been done.

Applications:

All acid plants for removal of SO₃ and acid mist.

Control Level Obtainable:

Extent of lime dust - SO₃ reaction unknown because of low temperature of acid plant tail gas.

Expected Relative Cost:

Capital Cost	Low
Operating Cost	Average

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown. Pilot testing required.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 4.1.1 - Absorption of NO_x and SO_2 with Solid MgSO_3 and MgO

Description:

Gases are passed upward through a bed of lump MgSO_3 - MgO . Water is sprayed downward to wet the surface of the sulfite to enhance the absorption reaction as well as to dissolve the sulfate formed. The sulfite reduces the NO_x to N_2 and SO_2 is neutralized by MgO .

Reduces:

NO_x to N_2 and removes SO_2 as MgSO_4 for disposal.

Status:

Idea

Patents:

None

Applications:

SO_2 and NO_x control for chamber acid plants.

Control Level Obtainable:

Unknown

Expected Relative Cost:

Capital Cost	Average
Operating Cost	Average-High

Reliability:

Operates independently. Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown. Would require piloting.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 4.1.2 - Reduction of NO_x and Absorption of SO₂ with Sulfite-Carbonate Solution

Description:

Nitrogen oxides and SO₂ are absorbed in a venturi scrubber using inorganic aqueous sulfite-carbonate solution. The NO_x is converted to N₂ and sulfites to sulfates. The SO₂ converts carbonates to sulfites.

Recovers:

NO_x and SO₂ in the form of N₂ + sulfate salt for disposal of sulfate salt. N₂ vented to atmosphere.

Status:

Tested

Patents:

British 1,134,881

Licensors:

Societa Industriale Catanese S.p.A., Palermo, Italy

Applications:

Chamber acid plant for SO₂ and NO_x control.

Control Level Obtainable:

NO_x to about 200 ppm; SO₂ <100 ppm.

Expected Relative Cost:

Capital Cost	Low-Average
Operating Cost	Average-High

Reliability:

Does not affect reliability of acid plant.

Estimated Overall Worth:

Unknown. Nitric oxide difficult to entrain for reduction. Scrubbing solution may require large excess of sulfite for efficient absorption. Piloting required.

Not presently feasible.

SULFURIC ACID PLANT
EMISSION CONTROL PROCESS SURVEY

No. 4.1.3 - Absorption of SO₂ and NO_x with Sodium Hydroxide

Description:

Nitrogen oxides and SO₂ are absorbed in NaOH, using two counter-current absorption towers in series, to form Na₂SO₃, NaNO₂ and NaNO₃. NaNO₂ catalyzes the oxidation of Na₂SO₃ to Na₂SO₄. The absorbent contains NaNO₃, NaNO₂, Na₂SO₄ and free NaOH.⁴ A bleed stream is evaporated and crystallized to produce a salt mixture for sale or disposal.

Recovers:

SO₂ and NO_x as a sodium salt mixture for sale or disposal.

Status:

Some laboratory work has been done.

Patents:

Probably

Applications:

SO₂ and NO_x control for chamber acid plants.

Control Level Obtainable:

200 ppm NO_x, 100 ppm SO₂.

Expected Relative Cost:

Capital Cost	Average-High
Operating Cost	High

Reliability:

Operates independently. Does not affect reliability of the acid plant.

Estimated Overall Worth:

Unknown.

Costly; not promising.

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-1
ESTIMATED CAPITAL COST
1.2.1/1.2 (250)

4,000 ppm INITIAL EMISSION LEVEL

500 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	
	-	SO ₂ Recovery	
	-	Sub Total	\$254,000
Civil Works			40,000
Buildings			-0-
Insulation			31,000
Piping and Ductwork			129,800
Instrumentation			14,400
Electrical			20,600
Miscellaneous and Catalyst			<u>23,000</u>
		Total	\$512,800

TABLE A-2
ESTIMATED CAPITAL COST
1.2.1/1.1 (250)

5,000 ppm INITIAL EMISSION LEVEL

500 ppm CONTROL EFFECTIVENESS

Equipment	-		\$254,000
Civil Works			40,500
Buildings			-0-
Insulation			31,000
Piping and Ductwork			130,000
Instrumentation			14,400
Electrical			20,500
Miscellaneous and Catalyst			<u>24,600</u>
		Total	\$515,000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-3
ESTIMATED CAPITAL COST

1. 2. 2/1. 1 (50)

5, 000 ppm INITIAL EMISSION LEVEL

500 ppm CONTROL EFFECTIVENESS

Equipment	\$134, 600
Civil Works	18, 700
Buildings	-0-
Insulation	13, 000
Piping and Ductwork	60, 000
Instrumentation	14, 600
Electrical	9, 700
Miscellaneous and Catalyst	<u>9, 400</u>
Total	\$260, 000

TABLE A-4
ESTIMATED CAPITAL COST

1. 2. 2/1. 2 (250)

4, 000 ppm INITIAL EMISSION LEVEL

500 ppm CONTROL EFFECTIVENESS

Equipment	\$236, 500
Civil Works	41, 200
Buildings	-0-
Insulation	26, 200
Piping and Ductwork	106, 400
Instrumentation	14, 400
Electrical	20, 700
Miscellaneous and Catalyst	<u>36, 700</u>
Total	\$482, 100

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-5
ESTIMATED CAPITAL COST
1.2.2/1.1 (250)
5,000 ppm INITIAL EMISSION LEVEL
500 ppm CONTROL EFFECTIVENESS

Equipment	\$234,000
Civil Works	41,500
Buildings	-0-
Insulation	26,100
Piping and Ductwork	105,500
Instrumentation	14,400
Electrical	20,500
Miscellaneous and Catalyst	<u>43,000</u>
Total	\$485,000

TABLE A-6
ESTIMATED CAPITAL COST
1.2.2/1.2 (750)
4,000 ppm INITIAL EMISSION LEVEL
500 ppm CONTROL EFFECTIVENESS

Equipment	\$465,000
Civil Works	66,300
Buildings	-0-
Insulation	59,500
Piping and Ductwork	185,000
Instrumentation	14,500
Electrical	24,500
Miscellaneous and Catalyst	<u>105,200</u>
Total	\$920,000

TABLE A-7
ESTIMATED CAPITAL COST
1.2.2/1.2 (1,500)
4,000 ppm INITIAL EMISSION LEVEL
500 ppm CONTROL EFFECTIVENESS

Equipment	\$713,000
Civil Works	112,000
Buildings	-0-
Insulation	82,000
Piping and Ductwork	309,000
Instrumentation	17,200
Electrical	27,700
Miscellaneous and Catalyst	<u>189,100</u>
Total	\$1,450,000

TABLE A-8
ESTIMATED CAPITAL COST
1.1.1 (750)
NEW DUAL ABSORPTION PLANT
(NO OLEUM PRODUCTION)

Equipment	\$1,288,000
Civil Works	187,500
Buildings	18,700
Insulation	89,200
Piping and Ductwork	452,000
Instrumentation	66,300
Electrical	104,000
Miscellaneous and Catalyst	<u>291,300</u>
Total	\$2,500,000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-9
ESTIMATED CAPITAL COST
PROCESS 1.2.3/1.4 (340)
3,200 ppm INITIAL EMISSION LEVEL
500 ppm CONTROL EFFECTIVENESS

Equipment	\$393,000
Civil Works	61,700
Buildings	-0-
Insulation	29,900
Piping and Ductwork	170,000
Instrumentation	18,400
Electrical	25,800
Miscellaneous	<u>41,200</u>
Total	\$740,000

TABLE A-10
ESTIMATED CAPITAL COST
PROCESS 2.1.1/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$ 22,700
	-	SO ₂ Recovery	<u>264,000</u>
	-	Sub Total	\$286,700
Civil Works			27,300
Buildings			97,200
Insulation			51,700
Piping and Ductwork			60,700
Instrumentation			30,300
Electrical			30,000
Miscellaneous			<u>6,100</u>
Total			\$590,000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-11
ESTIMATED CAPITAL COST
PROCESS 2.2.6/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$ 21,000
	-	SO ₂ Recovery	<u>212,300</u>
	-	Sub Total	\$233,300
Civil Works			25,000
Buildings			88,500
Insulation			47,600
Piping and Ductwork			55,400
Instrumentation			27,700
Electrical			27,000
Miscellaneous			<u>5,500</u>
		Total	\$510,000

TABLE A-12
ESTIMATED CAPITAL COST
PROCESS 2.2.8/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$ 88,400
	-	SO ₂ Recovery	<u>163,000</u>
	-	Sub Total	\$251,400
Civil Works			30,000
Buildings			86,500
Insulation			41,600
Piping and Ductwork			106,500
Instrumentation			33,000
Electrical			30,000
Miscellaneous			<u>6,000</u>
		Total	\$585,000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-13
ESTIMATED CAPITAL COST
PROCESS 2. 2. 14/1. 2 (250)
4, 000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$166, 000
	-	SO ₂ Recovery	67, 000
	-	Sub Total	\$233, 000
Civil Works			18, 600
Buildings			46, 300
Insulation			13, 900
Piping and Ductwork			71, 200
Instrumentation			53, 300
Electrical			23, 100
Miscellaneous			5, 600
		Total	\$465, 000

TABLE A-14
ESTIMATED CAPITAL COST
PROCESS 2. 2. 28/1. 2 (250)
4, 000 ppm INITIAL EMISSION LEVEL
500 ppm CONTROL EFFECTIVENESS

Equipment		\$320, 000
Civil Works		29, 700
Buildings		86, 000
Insulation		17, 200
Piping and Ductwork		112, 000
Instrumentation		58, 000
Electrical		38, 000
Miscellaneous		9, 100
	Total	\$670, 000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-15
ESTIMATED CAPITAL COST
PROCESS 2.3.3/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$ 46,800
	-	SO ₂ Recovery	84,300
	-	Sub Total	\$131,100
Civil Works			10,800
Buildings			32,000
Insulation			-0-
Piping and Ductwork			50,800
Instrumentation			15,400
Electrical			38,500
Miscellaneous			6,400
Total			\$285,000

TABLE A-16
ESTIMATED CAPITAL COST
PROCESS 2.4.5/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$133,000
	-	SO ₂ Recovery	243,000
	-	Sub Total	\$376,000
Civil Works			13,400
Buildings			53,700
Insulation			21,500
Piping and Ductwork			95,500
Instrumentation			40,300
Electrical			14,700
Miscellaneous			4,900
Total			\$620,000

Chemical Construction Corporation
CONSULTING DIVISION

TABLE A-17
ESTIMATED CAPITAL COST
PROCESS 2.4.6/1.2 (250)
4,000 ppm INITIAL EMISSION LEVEL
200 ppm CONTROL EFFECTIVENESS

Equipment	-	SO ₂ Removal	\$ 59,000
	-	SO ₂ Recovery	<u>271,000</u>
	-	Sub Total	\$330,000
Civil Works			15,300
Buildings			173,000
Insulation			21,600
Piping and Ductwork			61,900
Instrumentation			30,700
Electrical			46,000
Miscellaneous			<u>11,500</u>
		Total	\$690,000

TABLE B1

CONTROL COST FOR NEW DUAL ABSORPTION 1.1.1

COMPARED TO

CLASS 2.2 SINGLE ABSORPTION ACID PLANTS

Process	1.1.1 (250)	1.1.1 (750)	1.1.1 (1,500)
Nominal Capacity	250 T/D	750 T/D	1,500 T/D
Production Rate	250 T/D	750 T/D	1,500 T/D
Conversion Rate	99.5 %	99.5 %	99.5 %
Initial Investment	\$1,300,000	\$2,500,000	\$3,700,000
Book Value	1,300,000	2,500,000	3,700,000
Raw Material and Utilities			
Sulfur	\$ 677,700	\$2,033,000	\$4,066,000
Elec. Power	39,400	118,000	236,000
Cooling Water	24,700	74,100	148,200
Process Water	360	1,080	2,160
B. F. Water	5,900	17,700	35,400
Steam	- 59,800	- 179,300	- 359,400
Operating Expenses			
Labor	47,500	47,500	47,500
Supervision	21,100	21,100	21,100
Maintenance (4%)	52,000	100,000	148,000
Overhead @ 70% of Above	84,800	118,700	152,000
Indirect Costs			
Depreciation 10%	227,000	437,000	647,000
Interest 7-1/2%)			
Taxes and Insurance (1-1/2%)	19,500	37,500	55,500
Annual Operating Cost	\$1,140,160	\$2,826,380	\$5,199,460
T/Y Acid Production	82,500	247,500	495,000
Production Cost/T	\$ 13.84	\$ 11.43	\$ 10.50
Control Cost/T	.41	.18	.12

TABLE B2
CONTROL COST FOR ADD-ON DUAL ABSORPTION 1.2.1
APPLIED TO
CLASSES 1.1 OR 1.2 ACID PLANTS

Process	1.2.1/1.1 (250)	1.2.1/1.2 (250)
Initial Emission Level	5,000 ppm	4,000 ppm
Nominal Capacity	250 T/D	250 T/D
Production Rate	261.9 T/D	259.1 T/D
Conversion Rate	99.5 %	99.5 %
Initial Investment	\$1,615,000	\$1,612,800
Book Value	515,000	1,612,800
Raw Material and Utilities		
Sulfur	\$ 710,900	\$ 703,300
Elec. Power	57,800	57,600
Cooling Water	30,200	30,100
Process Water	350	340
B. F. Water	4,910	4,910
Steam	- 54,400	- 54,300
Operating Expenses		
Labor	47,500	47,500
Supervision	21,100	21,100
Maintenance (4%)	64,500	64,500
Overhead @ 70% of Above	93,200	93,200
Indirect Costs		
Depreciation 10%)	90,000	282,500
Interest 7-1/2%)		
Taxes and Insurance		
(1-1/2%)	24,200	24,200
Annual Operating Cost	\$1,090,260	\$1,274,950
T/Y Acid Production	86,427	85,503
Production Cost/T	\$ 12.61	\$ 14.91
Control Cost/T	1.44	1.48

TABLE B3

CONTROL COST FOR ADD-ON DUAL ABSORPTION 1,2,2

APPLIED TO

CLASS 1,1 ACID PLANTS AT 5,000 ppm EMISSION LEVEL

Process	No Supplementary Production			With Supplementary Production		
	1,2,2/1,1 (50)	1,2,2/1,1 (250)	1,2,2/1,1 (750)	1,2,2/1,1 (50)	1,2,2/1,1 (250)	1,2,2/1,1 (750)
Nominal Capacity	50 T/D	250 T/D	750 T/D	50 T/D	250 T/D	750 T/D
Production Rate	52.3 T/D	261.9 T/D	785 T/D	58 T/D	290.5 T/D	871 T/D
Conversion Rate	99.5 %	99.5 %	99.5 %	99.5 %	99.5 %	99.5 %
Initial Investment	\$ 685,000	\$ 1,585,000	\$ 3,020,000	\$ 685,000	\$ 1,535,000	\$ 3,020,000
Book Value	260,000	485,000	920,000	260,000	485,000	920,000
Raw Material and Utilities						
Sulfur	\$ 142,000	\$ 710,900	\$ 2,110,000	\$ 157,700	\$ 788,500	\$ 2,365,000
Elec. Power	11,570	57,800	172,700	12,450	62,100	186,000
Cooling Water	6,040	30,200	90,300	6,800	33,900	101,600
Process Water	70	350	1,020	80	380	1,140
B. F. Water	980	4,910	14,730	1,150	5,750	17,260
Steam	10,870	54,400	163,000	12,850	64,300	193,000
Operating Expenses						
Labor	47,500	47,500	47,500	47,500	47,500	47,500
Supervision	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	27,400	63,400	121,000	27,400	63,400	121,000
Overhead @ 70%	67,200	92,400	132,800	67,200	92,400	132,800
Indirect Costs						
Depreciation 10%	45,500	84,800	161,000	45,500	84,800	161,000
Interest 7-1/2%)						
Taxes and Insurance (1-1/2%)	10,270	23,800	45,200	10,270	23,800	45,200
Annual Operating Cost	\$ 368,760	\$ 1,082,760	\$ 2,754,350	\$ 384,360	\$ 1,159,330	\$ 3,006,600
T/Y Acid Production	17,250	86,427	259,000	19,140	95,865	287,430
Production Cost/T	\$ 21.35	\$ 12.53	\$ 10.62	\$ 20.08	\$ 12.09	\$ 10.46
Control Cost/T	3.50	1.36	.78	2.30	.92	.59

TABLE B4
CONTROL COST FOR ADD-ON DUAL ABSORPTION 1, 2, 2
APPLIED TO
CLASS 1, 2 ACID PLANTS

Process	Without Supplementary Production			With Supplementary Production		
	1, 2, 2/1, 2 (250)	1, 2, 2/1, 2 (250)	1, 2, 2/1, 2 (750)	1, 2, 2/1, 2 (250)	1, 2, 2/1, 2 (750)	1, 2, 2/1, 2 (1, 500)
Initial Emission Level	4, 000 ppm	2, 500 ppm	4, 000 ppm	4, 000 ppm	4, 000 ppm	4, 000 ppm
Nominal Capacity	250 T/D	250 T/D	750 T/D	250 T/D	750 T/D	1, 500 T/D
Production Rate	259.1 T/D	255 T/D	777 T/D	288 T/D	864 T/D	1, 727 T/D
Conversion Rate	99.5 %	99.5 %	99.5 %	99.5 %	99.5 %	99.5 %
Initial Investment	\$1, 582, 100	\$1, 580, 000	\$3, 020, 000	\$1, 582, 100	\$3, 020, 000	\$4, 450, 000
Book Value	1, 582, 100	1, 580, 000	3, 020, 000	1, 582, 100	3, 020, 000	4, 450, 000
Raw Material and Utilities						
Sulfur	\$ 703, 300	\$ 692, 000	\$2, 110, 000	\$ 781, 700	\$2, 345, 000	\$4, 690, 000
Elec. Power	57, 600	56, 700	173, 300	62, 900	188, 500	377, 500
Cooling Water	30, 100	29, 700	90, 600	34, 000	101, 700	204, 000
Process Water	340	340	1, 050	380	1, 140	2, 280
B. F. Water	4, 910	4, 830	14, 720	5, 750	17, 260	34, 500
Steam	- 54, 300	- 53, 500	- 163, 000	- 64, 300	- 193, 000	- 386, 000
Operating Expenses						
Labor	47, 500	47, 500	47, 500	47, 500	47, 500	47, 500
Supervision	21, 100	21, 100	21, 100	21, 100	21, 100	21, 100
Maintenance (4%)	63, 300	63, 300	121, 000	63, 300	121, 000	178, 000
Overhead @ 70% of Above	92, 300	92, 300	132, 800	92, 300	132, 800	172, 800
Indirect Costs						
Depreciation 10%)	277, 000	277, 000	529, 000	277, 000	529, 000	778, 000
Interest 7-1/2%)						
Taxes and Insurance (1-1/2%)	23, 700	23, 700	45, 200	23, 700	45, 200	66, 700
Annual Operating Cost	\$1, 266, 850	\$1, 254, 970	\$3, 123, 270	\$1, 345, 330	\$3, 357, 200	\$6, 186, 380
T/Y Acid Production	85, 503	84, 150	256, 500	95, 040	285, 000	570, 000
Production Cost/T	\$ 14.82	\$ 14.91	\$ 12.20	\$ 14.16	\$ 11.76	\$ 10.86
Control Cost/T	1.39	1.63	.95	.73	.51	.48

TABLE B5
CONTROL COST FOR ADD-ON DUAL ABSORPTION 1. 2. 3
APPLIED TO
CLASS 1. 4 SMELTER GAS ACID PLANT

Process	1. 2. 3/1. 4 (250)	1. 2. 3/1. 4 (340)
Initial Emission Level	3, 200 ppm	1, 800 ppm
Nominal Capacity	250 T/D	340 T/D
Production Rate	257 T/D	344. 5 T/D
Conversion Rate	99. 5 %	99. 5 %
Initial Investment	\$2, 320, 000	\$2, 740, 000
Book Value	2, 320, 000	2, 740, 000
Raw Material and Utilities		
S as SO ₂	\$ ---	\$ ---
Elec. Power	74, 500	99, 800
Cooling Water	57, 700	77, 300
Process Water	340	450
Natural Gas	14, 760	19, 800
Operating Expenses		
Labor	94, 300	94, 300
Supervision	21, 100	21, 100
Maintenance (4%)	92, 800	109, 600
Overhead @ 70% of Above	145, 700	157, 500
Indirect Costs		
Depreciation 10%)	406, 000	479, 500
Interest 7-1/2%)		
Taxes and Insurance (1-1/2%)	34, 800	41, 100
Annual Operating Cost	\$ 942, 000	\$1, 100, 450
T/Y Acid Production	84, 810	113, 685
Production Cost/T	\$ 11. 11	\$ 9. 68
Control Cost/T	2. 31	2. 22

TABLE B6
CONTROL COST FOR PROCESS 2.1.1
APPLIED TO
CLASS 1.1 and 1.2 ACID PLANTS

Process	2.1.1/1.1 (250)	2.1.1/1.2 (250)
Initial Emission Level	5,000 ppm	4,000 ppm
Nominal Capacity	250 T/D	250 T/D
Operating Capacity	250 T/D	250 T/D
Conversion Rate	99.75 %	99.8 %
Initial Investment	\$1,730,000	\$1,691,000
Book Value	630,000	1,691,000
Raw Material and Utilities		
Sulfur	\$ 709,000	\$ 702,700
Elec. Power	55,850	54,300
Cooling Water	24,700	24,700
Process Water	710	630
B.F. Water	5,770	5,770
Steam	- 54,300	- 56,300
Natural Gas	1,200	960
Na ₂ SO ₃	- 225,000	- 180,000
Na ₂ CO ₃	180,000	144,000
Oxidation Inhibitor	2,500	2,000
Operating Expenses		
Labor	111,000	111,000
Supervision	21,100	21,100
Maintenance (4%)	69,200	67,600
Overhead @ 70% of Above	141,000	140,000
Indirect Costs		
Depreciation 10%)	111,000	296,000
Interest 7-1/2%)		
Taxes and Insurance		
(1-1/2%)	26,000	25,440
Annual Operating Cost	\$1,179,730	\$1,359,900
T/Y Acid Production	82,500	82,500
Production Cost/T	\$ 14.30	\$ 16.48
Control Cost/T	3.13	3.05

TABLE B7

CONTROL COST (SO₂ CONTROL ONLY) FOR PROCESS 2.2.6

APPLIED TO

CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process	2.2.6/1.2 (50)	2.2.6/1.2 (250)	2.2.6/1.2 (250)	2.2.6/1.2 (250)	2.2.6/1.2 (250)	2.2.6/1.1 (250)	2.2.6/1.4 (250)	2.2.6/1.2 (750)	2.2.6/1.2 (1,500)
Initial Emission									
Level	4,000 ppm	4,000 ppm	2,000 ppm	2,500 ppm	5,000 ppm	5,000 ppm	3,200 ppm	4,000 ppm	4,000 ppm
Nominal Capacity	50 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	750 T/D	1,500 T/D
Production Rate	52 T/D	260 T/D	256 T/D	261 T/D	262 T/D	262 T/D	257 T/D	780 T/D	1,560 T/D
Conversion Rate	99.8 %	99.8 %	99.9 %	98.875 %	99.75 %	99.75 %	99.84 %	99.8 %	99.8 %
Initial Investment	\$720,000	\$1,610,000	\$1,565,000	\$1,570,000	\$1,650,000	\$1,650,000	\$2,275,000	\$2,880,000	\$4,045,000
Book Value	720,000	1,610,000	1,565,000	1,570,000	1,650,000	1,650,000	2,275,000	2,880,000	4,045,000
Raw Material and Utilities									
Sulfur	\$140,500	\$ 702,700	\$ 693,000	\$ 692,000	\$ 709,000	\$ 709,000	\$ -0-	\$2,107,000	\$ 4,214,000
S as SO ₂									
Elec. Power	8,600	42,900	42,700	42,300	44,600	44,600	48,600	128,700	257,400
Cooling Water	5,200	25,300	25,400	25,400	26,000	26,000	26,000	77,300	154,600
Process Water	70	330	330	330	330	330	330	990	1,980
B.F. Water	1,160	5,770	5,770	5,770	5,820	5,770	5,770	17,300	34,600
Steam	-12,850	64,200	-	63,200	64,800	64,200	35,000	-192,400	-384,800
Fuel Oil	5,600	25,800	17,500	17,500	35,000	35,000	35,000	84,000	168,000
MgO	200	990	625	620	1,250	1,250	1,250	2,970	5,940
Operating Expenses									
Labor	94,300	94,300	94,300	94,300	94,300	94,300	141,000	94,300	94,300
Supervision	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	28,800	64,300	62,600	62,600	66,000	66,000	91,000	115,000	161,800
Overhead @ 70% of Above									
Indirect Costs	100,940	125,700	124,600	124,700	127,000	127,000	177,300	161,420	194,040
Indirect Costs									
Depreciation 10% Interest 7-1/2%)	126,000	282,000	274,000	275,000	288,750	288,750	398,500	504,000	707,875
Taxes & Insurance (1-1/2%)	10,800	24,100	23,450	23,500	24,700	24,700	34,100	43,200	60,675
Annual Operating Cost	\$530,420	\$1,353,790	\$1,321,175	\$1,321,850	\$1,379,050	\$1,379,050	\$ 974,180	\$3,165,080	\$5,691,510
T/Y Acid Production	17,160	85,700	84,500	84,500	86,500	86,500	84,800	257,400	514,800
Production Cost/T	\$ 30.91	\$ 15.80	\$ 15.64	\$ 15.64	\$ 15.94	\$ 15.94	\$ 11.49	\$ 12.30	\$ 11.06
Control Cost/T	8.61	2.37	2.35	2.36	2.38	2.57	2.70	1.05	.68

TABLE B8
CONTROL COST (SO₂, SO₃ AND MIST) FOR PROCESS 2.2.6
APPLIED TO
CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process	2.2.6/1.2 (50)	2.2.6/1.2 (50)	2.2.6/1.1 (250)	2.2.6/1.2 (250)	2.2.6/1.2 (250)	2.2.6/1.4 (250)	2.2.6/1.2 (750)	2.2.6/1.2 (1500)	2.2.6/1.2 (1500)
Initial Emission Level	4,000 ppm	2,500 ppm	5,000 ppm	4,000 ppm	3,200 ppm	2,500 ppm	4,000 ppm	2,500 ppm	4,000 ppm
Nominal Capacity	50 T/D	50 T/D	250 T/D	250 T/D	250 T/D	250 T/D	750 T/D	1,500 T/D	1,500 T/D
Production Rate	52 T/D	51.2 T/D	262 T/D	256.1 T/D	257 T/D	257 T/D	768.3 T/D	1,536.5 T/D	1,560 T/D
Conversion Rate	99.8 %	99.875 %	99.75 %	99.8 %	99.84 %	99.875 %	99.8 %	99.875 %	99.8 %
Initial Investment	\$728,000	\$698,000	\$1,670,000	\$1,630,000	\$2,300,000	\$2,800,000	\$2,919,000	\$3,950,000	\$4,104,000
Book Value	728,000	698,000	570,000	1,630,000	2,300,000	2,800,000	2,919,000	3,950,000	4,104,000
Raw Material and Utilities									
Sulfur	\$140,500	\$138,200	\$709,000	\$702,700	\$-	\$2,073,000	\$2,107,000	\$4,146,000	\$4,214,000
S as SO ₂									
Elec. Power	10,200	10,100	52,900	51,200	61,500	151,500	152,500	303,000	305,000
Cooling Water	5,200	5,120	26,000	25,400	26,000	76,000	77,300	152,200	154,600
Process Water	70	70	330	330	330	980	990	1,950	1,980
B. F. Water	1,160	1,140	5,770	5,700	5,770	17,100	17,300	34,100	34,600
Steam	-12,850	-12,650	-64,200	-64,200	-64,200	-189,500	-192,400	-379,000	-384,800
Fuel Oil	5,600	3,500	35,000	28,000	35,000	52,563	84,000	105,000	168,000
MgO	200	125	1,250	990	1,250	1,860	2,970	3,710	5,940
Operating Expenses									
Labor	94,300	94,300	94,300	94,300	141,000	94,300	94,300	94,300	94,300
Supervision	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	29,120	27,920	66,700	65,200	92,000	112,000	116,760	158,000	164,200
Overhead @ 70% of Above	101,160	100,300	127,500	126,400	178,000	159,200	162,500	191,400	195,720
Indirect Costs									
Depreciation 10%	127,400	122,150	99,000	285,000	403,000	490,000	510,800	691,250	718,200
Interest 7-1/2%									
Taxes & Insurance (1-1/2%)	10,920	10,470	25,100	24,500	34,500	42,000	43,800	59,250	61,560
Annual Operating Cost	\$534,080	\$521,845	\$1,200,550	\$1,367,090	\$993,680	\$3,102,040	\$3,198,920	\$5,582,260	\$5,754,400
T.Y. Acid Production	17,160	16,900	86,506	85,700	84,800	253,540	257,400	507,045	514,800
Production Cost/T	\$31.12	\$30.38	\$13.88	\$15.79	\$11.72	\$12.23	\$12.43	\$11.01	\$11.18
Control Cost/T	3.82	8.70	2.71	2.51	2.92	1.15	1.18	.78	.80

TABLE B9

CONTROL COST FOR PROCESS 2.2.8

APPLIED TO

CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process	2.2.8/1.1 (250)	2.2.8/1.2 (250)	2.2.8/1.4 (250)
Initial Emission Level	5,000 ppm	4,000 ppm	3,200 ppm
Nominal Capacity	250 T/D	250 T/D	250 T/D
Production Rate	262 T/D	260 T/D	257 T/D
Conversion Rate	99.75 %	99.8 %	99.84 %
Initial Investment	\$1,710,000	\$1,685,000	\$2,340,000
Book Value	610,000	1,685,000	2,340,000
Raw Material and Utilities			
Sulfur	\$ 709,000	\$ 702,700	\$ -0-
S as SO ₂			64,900
Elec. Power	56,330	55,750	25,300
Cooling Water	25,300	25,200	500
Process Water	500	600	5,770
B.F. Water	5,770	5,770	-
Steam	-	51,000	47,700
K ₂ CO ₃	14,300	11,400	14,300
Oxidation Inhibitor	2,960	2,360	2,960
Operating Expenses			
Labor	95,000	95,000	141,000
Supervision	21,100	21,100	21,100
Maintenance (4%)	68,300	67,300	93,500
Overhead @ 70% of Above	129,200	128,400	179,000
Indirect Costs			
Depreciation 10%)	106,800	295,000	410,000
Interest 7-1/2%)			
Taxes and Insurance (1-1/2%)	25,600	25,300	35,100
Annual Operating Cost	\$1,212,460	\$1,384,880	\$ 945,730
T/Y Acid Production	86,500	85,700	84,800
Production Cost/T	\$ 14.02	\$ 16.16	\$ 11.15
Control Cost/T	2.84	2.73	2.25

TABLE B10
CONTROL COST FOR PROCESS 2.2.14
APPLIED TO
CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process /	2.2.14/1.2 (50)	2.2.14/1.1 (250)	2.2.14/1.2 (250)	2.2.14/1.4 (250)	2.2.14/1.2 (750)	2.2.14/1.2 (1,500)
Initial Emission Level	4,000 ppm	5,000 ppm	4,000 ppm	3,200 ppm	4,000 ppm	4,000 ppm
Nominal Capacity	50 T/D	250 T/D	250 T/D	250 T/D	750 T/D	1,500 T/D
Production Rate	52 T/D	262 T/D	260 T/D	257 T/D	780 T/D	1,560 T/D
Conversion Rate	99.8 %	99.75 %	99.8 %	99.84 %	99.8 %	99.8 %
Initial Investment	\$ 695,000	\$ 1,575,000	\$ 1,565,000	\$ 2,235,000	\$ 2,865,000	\$ 4,080,000
Book Value	695,000	475,000	1,565,000	2,235,000	2,865,000	4,080,000
Raw Material and Utilities						
Sulfur	\$ 140,500	\$ 709,000	\$ 702,700	\$ -0-	\$ 2,107,000	\$ 4,214,000
S as SO ₂	11,500	57,250	57,200	72,500	172,000	344,000
Elec. Power	5,300	26,900	26,460	50,100	79,300	159,000
Cooling Water	80	380	370	380	1,100	2,200
Process Water	1,150	5,770	5,770	21,800	17,300	34,600
B. F. Water	9,350	42,400	46,750	11,900	140,000	280,000
Steam	1,900	11,900	9,500	11,900	28,500	57,000
Methylamine	120	750	600	750	1,800	3,600
Antioxidant						
Operating Expenses						
Labor	71,200	71,200	71,200	111,500	71,200	71,200
Supervision	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	27,800	62,900	62,700	89,400	115,600	163,500
Overhead @ 70% of Above	84,000	108,500	108,500	160,500	145,000	179,000
Indirect Costs						
Depreciation 10%	121,500	83,000	274,000	391,500	501,000	715,000
Interest 7-1/2%)						
Taxes and Insurance (1-1/2%)	10,400	23,600	23,500	33,600	43,000	61,200
Annual Operating Cost	\$ 487,200	\$ 1,139,850	\$ 1,316,850	\$ 965,430	\$ 3,163,900	\$ 5,745,400
T/Y Acid Production	17,160	86,500	85,700	84,800	257,400	514,800
Production Cost/T	\$ 28.39	\$ 13.18	\$ 15.37	\$ 11.38	\$ 12.29	\$ 11.16
Control Cost/T	6.10	1.98	1.88	2.58	1.03	.78

TABLE B-11
CONTROL COST FOR PROCESS 2.2.22
APPLIED TO
CLASS 1.2 ACID PLANT

Process	2.2.22/1.2 (396)
Initial Emission Level	1,800 ppm
Nominal Capacity	396 ST/D
Production Rate	402 ST/D
Conversion Rate	99.82 %
Initial Investment	\$1,800,000
Book Value	1,800,000
Raw Material and Utilities	
Sulfur	\$1,105,000
Elec. Power	74,900
Cooling Water	39,500
Process Water	1,130
B. F. Water	9,250
Steam	- 77,400
Operating Expenses	
Labor	71,100
Supervision	21,100
Maintenance (4%)	72,000
Overhead @ 70% of Above	115,000
Indirect Costs	
Depreciation 10%)	315,000
Interest 7-1/2%)	
Taxes and Insurance (1-1/2%)	27,000
Annual Operating Cost	\$1,773,580
T/Y Acid Production	132,800
Production Cost/T	\$ 13.35
Control Cost/T	1.00

NOTE:

No information was available to determine control cost at conditions for which other processes were rated.

1,800 ppm would be an unusually low emission level for most U.S. plants.

TABLE B12

CONTROL COST FOR PROCESS 2.2.28

APPLIED TO

CLASS 1.1 and 1.2 ACID PLANTS

Process	2.2.28/1.1 (250)	2.2.28/1.1 (250)	2.2.28/1.2 (250)
Initial Emission Level	5,000 ppm	5,000 ppm	4,000 ppm
Nominal Capacity	250 T/D	250 T/D	250 T/D
Production Rate	262 T/D	263 T/D	260 T/D
Conversion Rate	99.5 %	99.75 %	99.8 %
Initial Investment	\$1,770,000	\$1,800,000	\$1,800,000
Book Value	670,000	700,000	1,800,000
Raw Material and Utilities			
Sulfur	\$ 709,000	\$ 709,000	\$ 705,700
S as SO ₂			
Elec. Power	44,000	44,000	44,000
Cooling Water	34,700	34,700	34,700
Process Water	480	480	480
B.F. Water	5,770	5,770	5,770
Steam	- 57,100	- 57,100	- 57,100
By-Product (Waste)	1,400	1,400	1,400
Al ₂ (SO ₄) ₃	2,200	2,200	2,200
CaSO ₄	1,600	1,600	1,600
CaCO ₃	7,500	7,500	7,500
Operating Expenses			
Labor	94,300	94,300	94,300
Supervision	21,100	21,100	21,100
Maintenance (4%)	70,700	72,000	72,000
Overhead @ 70% of Above	130,300	131,300	131,300
Indirect Costs			
Depreciation: 10%	117,200	122,500	315,000
Interest 7-1/2%)			
Taxes and Insurance (1-1/2%)	26,500	27,000	27,000
Annual Operating Cost	\$1,209,650	\$1,217,750	\$1,406,950
T/Y Acid Production	86,400	86,800	85,800
Production Cost/T	\$ 14.00	\$ 14.03	\$ 16.40
Control Cost/T	2.87	2.91	2.96

TABLE B13
CONTROL COST FOR PROCESS 2, 2, 29
APPLIED TO
CLASS 1, 1 and CLASS 1, 2 ACID PLANTS

	2, 2, 29/1, 2 (50)	2, 2, 29/1, 1 (250)	2, 2, 29, 1, 2 (250)	2, 2, 29/1, 2 (750)	2, 2, 29/1, 2 (1,500)
Process					
Initial Emission Level	4,000 ppm	5,000 ppm	4,000 ppm	4,000 ppm	4,000 ppm
Nominal Capacity	50 T/D	250 T/D	250 T/D	750 T/D	1,500 T/D
Production Rate	52.1 T/D	262 T/D	261 T/D	781 T/D	1,562 T/D
Conversion Rate	100 %	100 %	100 %	100 %	100 %
Initial Investment	\$ 620,000	\$ 1,495,000	\$ 1,542,000	\$ 2,970,000	\$ 4,312,000
Book Value	620,000	305,000	1,542,000	2,970,000	4,312,000
Raw Material and Utilities					
Sulfur	\$ 140,400	\$ 705,000	\$ 702,000	\$ 2,105,000	\$ 4,210,000
Elec. Power	10,700	53,600	53,600	161,000	322,000
Cooling Water	7,250	36,300	36,300	108,800	217,600
Process Water	70	350	350	1,050	2,100
B. F. Water	1,150	5,770	5,770	17,300	34,600
Steam	11,070	55,400	55,400	166,400	332,800
Resin	2,500	12,500	12,500	37,500	75,000
Alkali	250	1,250	1,250	3,750	7,500
Operating Expenses					
Labor	63,300	63,300	63,300	63,300	63,300
Supervision	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	24,800	55,800	61,700	115,000	181,600
Overhead @ 70% of Above	76,500	101,000	102,400	142,500	172,300
Indirect Costs					
Depreciation 10%	108,500	69,100	270,000	520,000	755,000
Interest 7-1/2%					
Taxes and Insurance (1-1/2%)	9,300	22,400	23,200	45,500	64,700
Annual Operating Cost	\$ 454,750	\$ 1,096,070	\$ 1,298,070	\$ 3,179,400	\$ 5,794,000
T/Y Acid Production	17,200	86,500	86,200	258,000	515,500
Production Cost/T	\$ 26.44	\$ 12.67	\$ 15.06	\$ 12.32	\$ 11.24
Control Cost/T	4.15	1.50	1.63	1.08	.86

TABLE B14
CONTROL COST FOR PROCESS 2, 3, 3
CLASS 1, 1, 1, 2 and 1, 4 (SMELTER GAS) ACID PLANTS
APPLIED TO

Process	2, 3, 3/1, 2 (50)	2, 3, 3/1, 1 (250)	2, 3, 3/1, 2 (250)	2, 3, 3/1, 4 (250)	2, 3, 3/1, 2 (750)	2, 3, 3/1, 2 (1, 500)
Initial Emission						
Level	4, 000 ppm	5, 000 ppm	4, 000 ppm	3, 200 ppm	4, 000 ppm	4, 000 ppm
Nominal Capacity	50 T/D	250 T/D	250 T/D	250 T/D	750 T/D	1, 500 T/D
Production Rate	50 T/D	250 T/D	250 T/D	250 T/D	750 T/D	1, 500 T/D
Conversion Rate	96 %	95 %	96 %	96, 8 %	96 %	96 %
Initial Investment	\$ 605, 000	\$1, 395, 000	\$1, 385, 000	\$2, 010, 000	\$2, 525, 000	\$3, 570, 000
Book Value	605, 000	295, 000	1, 385, 000	2, 010, 000	2, 525, 000	3, 570, 000
Raw Material and Utilities						
Sulfur	\$ 140, 500	\$ 709, 000	\$ 702, 700	\$ -0-	\$2, 105, 000	\$4, 110, 000
S as SO ₂						
Elec. Power	10, 000	50, 000	50, 700	62, 100	150, 300	300, 600
Cooling Water	4, 950	24, 700	24, 700	47, 900	74, 000	148, 000
Process Water	70	360	360	360	1, 080	2, 160
B. F. Water	1, 150	5, 770	5, 770	5, 770	18, 300	36, 600
Steam	-	-	-	-	-	-
CaSO ₄ (Waste)	12, 340	64, 200	64, 200	17, 500	182, 500	385, 000
CaO	2, 760	17, 500	13, 900	46, 400	41, 700	83, 400
	7, 420	46, 400	37, 100		111, 300	222, 600
Operating Expenses						
Labor	71, 200	71, 200	71, 200	500	71, 200	71, 200
Supervision	21, 100	21, 100	21, 100	21, 100	21, 100	21, 100
Maintenance (4%)	24, 200	55, 800	55, 400	80, 400	101, 000	143, 000
Overhead @ 70% of Above	81, 500	103, 700	103, 400	153, 900	135, 400	164, 800
Indirect Costs						
Depreciation 10%	106, 000	51, 600	242, 400	352, 000	442, 000	624, 500
Interest 7-1/2%)						
Taxes and Insurance (1-1/2%)	9, 070	21, 000	20, 800	30, 200	37, 900	53, 500
Annual Operating Cost	\$ 467, 100	\$1, 113, 930	\$1, 285, 330	\$ 930, 360	\$3, 117, 780	\$5, 596, 460
T/Y Acid Production	16, 500	82, 500	82, 500	82, 500	247, 500	495, 000
Production Cost/T	\$ 28. 31	\$ 13. 50	\$ 15. 58	\$ 11. 28	\$ 12. 60	\$ 11. 31
Control Cost/T	6. 00	2. 33	2. 14	2. 48	1. 33	. 94

TABLE B15

CONTROL COST FOR PROCESS 2.4.5

APPLIED TO

CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process	2.4.5/1.1 (250)	2.4.5/1.2 (250)	2.4.5/1.4 (250)
Initial Emission Level	5,000 ppm	4,000 ppm	3,200 ppm
Nominal Capacity	250 T/D	250 T/D	250 T/D
Production Rate	256.5 T/D	255 T/D	256.5 T/D
Conversion Rate	99.5 %	99.6 %	99.68 %
Initial Investment	\$1,750,000	\$1,720,000	\$2,400,000
Book Value	650,000	1,720,000	2,400,000
Raw Material and Utilities			
Sulfur	\$ 709,000	\$ 702,700	\$ ---
S as SO ₂	---		
Elec. Power	52,000	51,600	64,500
Cooling Water	25,400	25,400	47,900
Process Water	520	520	520
B. F. Water	5,770	5,770	
Steam	- 59,400	- 60,400	5,000
Ammonium Nitrate Solution	- 222,800	- 186,000	- 222,800
Ammonia	59,200	46,500	59,200
HNO ₃ (100%)	135,100	108,200	135,100
Oxidation Inhibitor	6,200	5,100	6,200
Operating Expenses			
Labor	95,000	95,000	142,500
Supervision	21,100	21,100	21,100
Maintenance (4%)	70,000	68,700	96,000
Overhead @ 70% of Above	130,500	129,200	181,700
Indirect Costs			
Depreciation 10%	114,000	301,000	420,000
Interest 7-1/2%)			
Taxes and Insurance (1-1/2%)	26,250	25,800	36,000
Annual Operating Cost	\$1,167,840	\$1,340,190	\$ 992,920
T/Y Acid Production	84,600	84,100	83,800
Production Cost/T	\$ 13.80	\$ 15.94	\$ 11.85
Control Cost/T	2.63	2.52	3.05

TABLE B16

CONTROL COST FOR PROCESS 2.4.6

APPLIED TO

CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS

Process	2.4.6/1.1 (250)	2.4.6/1.2 (250)	2.4.6/1.4 (250)
Initial Emission Level	5,000 ppm	4,000 ppm	3,200 ppm
Nominal Capacity	250 T/D	250 T/D	250 T/D
Production Rate	256.5 T/D	255 T/D	256.5 T/D
Conversion Rate	99.5 %	99.6 %	99.68 %
Initial Investment	\$1,850,000	\$1,790,000	\$2,470,000
Book Value	750,000	1,790,000	2,470,000
Raw Material and Utilities			
Sulfur	\$ 709,000	\$ 702,700	\$ -
S as SO ₂			-0-
Elec. Power	53,850	53,850	65,900
Cooling Water	24,750	24,730	47,950
Process Water	330	330	330
B.F. Water	5,770	5,770	---
Steam	- 62,900	- 62,100	- 2,610
Natural Gas	1,600	1,270	1,600
CaSO ₄ · 1/2H ₂ O	- 18,600	- 14,850	- 18,600
MnSO ₄	5,750	4,700	5,750
Lime	11,430	9,150	11,430
Operating Expenses			
Labor	111,000	111,000	156,500
Supervision	21,100	21,100	21,100
Maintenance (4%)	74,000	71,500	98,700
Overhead @ 70% of Above	144,300	142,500	193,500
Indirect Costs			
Depreciation 10%)	131,000	313,000	433,000
Interest 7-1/2%)			
Taxes and Insurance (1-1/2%)	27,770	26,850	37,100
Annual Operating Cost	\$1,240,150	\$1,411,500	\$1,051,650
T/Y Acid Production	84,600	84,200	83,700
Production Cost/T	\$ 14.66	\$ 16.76	\$ 12.56
Control Cost/T	3.50	3.33	3.76

TABLE B.7
ACID MIST CONTROL COST FOR DUAL MIST PAD SYSTEM 3.1.1

APPLIED TO

CLASSES 1, 1.1, 1.2, 2.2 and 1.4 (SMELTER GAS) PLANTS

	Mist Reduction from 20 to 2 Mg/SCF for Non-Oleum Plants				Mist Reduction from 50 to 5 Mg/SCF for Oleum Plants			
	3.1.1/1.2 (250)	3.1.1/2.2 (250)	3.1.1/1.1 (250)	3.1.1/1.4 (250)	3.1.1/1.2 (250)	3.1.1/2.2 (250)	3.1.1/1.1 (250)	3.1.1/1.4 (250)
Process	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D
Nominal Capacity	250.49 T/D	250.49 T/D	250.49 T/D	250.75 T/D	251.2 T/D	251.2 T/D	251.2 T/D	251.9 T/D
Production Rate	96 %	96 %	95 %	96.8 %	96 %	96 %	95 %	96.8 %
Conversion Rate	\$1,125,000	\$1,120,000	\$1,125,000	\$1,727,000	\$1,225,000	\$1,220,000	\$1,225,000	\$1,827,000
Initial Investment	1,125,000	1,120,000	25,000	1,727,000	1,225,000	1,220,000	25,000	1,827,000
Book Value								
Raw Material and Utilities								
Sulfur	\$ 702,700	\$ 702,700	\$ 709,000	\$	\$ 702,700	\$ 702,700	\$ 709,000	\$
S as SO ₂	40,000	40,000	40,000	47,000	40,000	40,000	40,000	47,000
Elec. Power	24,700	24,700	24,700	47,900	24,700	24,700	24,700	47,900
Cooling Water	330	330	330	330	330	330	330	330
Process Water	5,770	5,770	5,770		5,770	5,770	5,770	
B. F. Water	64,200	64,200	64,200		64,200	64,200	64,200	
Steam								
Operating Expenses								
Labor	47,500	47,500	47,500	94,300	47,500	47,500	47,500	94,300
Supervision	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	45,000	44,800	45,000	69,080	49,000	48,800	49,000	73,100
Overhead @ 70% of Above	79,520	79,380	79,520	129,140	82,300	82,200	82,300	131,900
Indirect Costs								
Depreciation 10%	196,875	196,000	4,375	302,225	214,700	213,500	4,375	319,000
Interest 7-1/2%)								
Taxes & Insurance (1-1/2%)	16,875	16,800	16,875	25,905	18,400	18,300	18,400	27,400
Annual Operating Cost	\$1,116,170	\$1,114,880	\$ 929,970	\$ 736,980	\$1,142,300	\$1,140,700	\$ 938,275	\$ 762,030
T/Y Acid Production	82,660	82,660	82,660	82,747	82,900	82,900	82,900	83,127
Production Cost/T	\$ 13.50	\$ 13.49	\$ 11.25	\$ 8.91	\$ 13.78	\$ 13.76	\$ 11.32	\$ 9.17
Control Cost/T	.07	.06	.08	.11	.04	.02	.06	.05

TABLE B18
ACID MIST CONTROL COST FOR SYSTEM 3.1.2

	APPLIED TO									
	CLASSES 1.1, 1.2, 2.2, 1.4 and 2.4 (SMELTER GAS) PLANTS									
	Mist Reduction from 20 to 0.3 Mg/SCF from Non-Oleum Plants					Mist Reduction from 50 Mg/SCF to 0.3 Mg/SCF for Oleum Plants				
Process	3.1, 2/1.1 (250)	3.1, 2/1.2 (250)	3.1, 2/2.2 (250)	3.1, 2/1.4 (250)	3.1, 2/2.4 (250)	3.1, 2/1.2 (250)	3.1, 2/2.2 (250)	3.1, 2/2.2 (250)	3.1, 2/2.2 (250)	3.1, 2/2.2 (250)
Nominal Capacity	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D	250 T/D
Production Rate	250, 52 T/D	250, 52 T/D	250, 52 T/D	250, 52 T/D	250, 82 T/D	250, 52 T/D	250, 82 T/D	250, 82 T/D	250, 82 T/D	250, 82 T/D
Conversion Rate	95 %	96 %	96 %	96 %	96 %	96 %	96 %	96 %	96 %	96 %
Initial Investment	\$1,200,000	\$1,200,000	\$1,170,000	\$1,827,000	\$1,790,000	\$1,300,000	\$1,300,000	\$1,300,000	\$1,300,000	\$1,270,000
Book Value	100,000	1,200,000	1,170,000	1,827,000	1,790,000	1,300,000	1,300,000	1,300,000	1,300,000	1,270,000
Raw Material and Utilities										
Sulfur	\$ 709,000	\$ 702,700	\$ 702,700	\$ ---	\$ ---	\$ 702,700	\$ 702,700	\$ 702,700	\$ 702,700	\$ 702,700
S as SO ₂										
Elec. Power	41,700	41,700	40,300	49,600	47,400	41,700	41,700	41,700	41,700	40,300
Cooling Water	24,700	24,700	24,700	47,900	47,900	24,700	24,700	24,700	24,700	24,700
Process Water	330	330	330	330	330	330	330	330	330	330
B.F. Water	5,770	5,770	5,770			5,770	5,770	5,770	5,770	5,770
Steam	- 64,200	- 64,200	- 64,200			- 64,200	- 64,200	- 64,200	- 64,200	- 64,200
Operating Expenses										
Labor	47,500	47,500	47,500	94,300	94,300	47,500	47,500	47,500	47,500	47,500
Supervision	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	48,000	48,000	46,800	73,000	71,600	52,000	52,000	52,000	52,000	50,800
Overhead @ 70%										
of Above	81,600	81,600	80,800	132,100	131,000	84,400	84,400	84,400	84,400	83,600
Indirect Costs										
Depreciation 10%)	17,500	210,000	204,750	320,000	313,500	227,500	227,500	227,500	227,500	222,500
Interest 7-1/2%)										
Taxes & Insurance (1-1/2%)	18,000	18,000	17,550	27,400	26,800	19,500	19,500	19,500	19,500	19,050
Annual Operating Cost	\$ 951,000	\$1,137,200	\$1,128,100	\$ 765,730	\$ 753,930	\$1,163,000	\$1,163,000	\$1,163,000	\$1,163,000	\$1,154,150
T/Y Acid Production	82,670	82,670	82,670	82,770	82,770	82,770	82,770	82,770	82,770	82,940
Production Cost/T	\$ 11.50	\$ 13.76	\$ 13.65	\$ 9.25	\$ 9.11	\$ 14.02	\$ 14.02	\$ 14.02	\$ 14.02	\$ 13.92
Control Cost/T	.33	.33	.22	.45	.31	.28	.28	.28	.28	.18

TABLE B19
ACID MIST CONTROL COST FOR SYSTEM 3.1.3
APPLIED TO
CLASSES 1.1, 1.2, 2.2, 1.4 and 2.4 (SMELTER GAS) ACID PLANTS

Process	Mist Reduction from 20 to 0.5 Mg/SCF for Non-Oleum Plants										Mist Reduction from 50 to 0.5 Mg/SCF for Oleum Plants									
	3.1.3/1.1 (250) 250 T/D	3.1.3/1.2 (250) 250 T/D	3.1.3/2.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.4 (250) 250 T/D	3.1.3/1.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.4 (250) 250 T/D	3.1.3/1.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.4 (250) 250 T/D	3.1.3/1.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.2 (250) 250 T/D	3.1.3/1.4 (250) 250 T/D	3.1.3/2.4 (250) 250 T/D
Nominal Capacity	250.51 T/D	250.51 T/D	250.51 T/D	250.81 T/D	250.81 T/D	250.51 T/D	250.81 T/D	250.51 T/D	250.81 T/D	250.81 T/D	250.51 T/D	250.81 T/D	250.51 T/D	250.81 T/D	252.1 T/D	250.51 T/D	250.81 T/D	250.51 T/D	250.81 T/D	252.1 T/D
Conversion Rate	95 %	96 %	96 %	96.8 %	96.8 %	96 %	96.8 %	96 %	96.8 %	96.8 %	96 %	96.8 %	96 %	96.8 %	96.8 %	96 %	96.8 %	96 %	96.8 %	96.8 %
Initial Investment	\$1,144,000	\$1,144,000	\$1,123,000	\$1,764,000	\$1,732,000	\$1,144,000	\$1,732,000	\$1,123,000	\$1,764,000	\$1,732,000	\$1,144,000	\$1,732,000	\$1,123,000	\$1,764,000	\$1,864,000	\$1,144,000	\$1,732,000	\$1,123,000	\$1,764,000	\$1,864,000
Book Value	44,000	1,144,000	1,123,000	1,764,000	1,732,000	1,144,000	1,732,000	1,123,000	1,764,000	1,732,000	1,144,000	1,732,000	1,123,000	1,764,000	1,864,000	1,144,000	1,732,000	1,123,000	1,764,000	1,864,000
Raw Material and Utilities																				
Sulfur	\$709,000	\$702,700	\$702,700	\$	\$	\$702,700	\$	\$702,700	\$	\$	\$702,700	\$	\$702,700	\$	\$	\$702,700	\$	\$702,700	\$	\$
S as SO ₂																				
Elec. Power	40,700	40,700	39,400	48,100	45,900	40,700	45,900	39,400	48,100	45,900	40,700	45,900	39,400	48,100	45,900	40,700	45,900	39,400	48,100	45,900
Cooling Water	24,700	24,700	24,700	47,900	47,900	24,700	47,900	24,700	47,900	47,900	24,700	47,900	24,700	47,900	47,900	24,700	47,900	24,700	47,900	47,900
Process Water	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330	330
B.F. Water	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770	5,770
Steam	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200	64,200
Operating Expenses																				
Labor	47,500	47,500	47,500	94,300	94,300	47,500	94,300	47,500	94,300	94,300	47,500	94,300	47,500	94,300	94,300	47,500	94,300	47,500	94,300	94,300
Supervision	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	45,700	45,700	45,000	70,600	69,300	45,000	69,300	45,000	70,600	69,300	45,000	69,300	45,000	70,600	73,300	45,000	69,300	45,000	70,600	73,300
Overhead @ 70% of Above	80,000	80,000	79,500	130,000	129,200	79,500	129,200	79,500	130,000	129,200	79,500	129,200	79,500	130,000	132,800	79,500	129,200	79,500	130,000	132,800
Indirect Costs																				
Depreciation 10%																				
Interest 7-1/2%	7,700	200,500	196,700	308,500	303,000	200,500	303,000	196,700	308,500	303,000	200,500	303,000	196,700	308,500	326,000	200,500	303,000	196,700	308,500	326,000
Taxes & Insurance (1-1/2%)	17,150	17,150	16,870	26,450	26,000	17,150	26,450	16,870	26,450	26,000	17,150	26,450	16,870	26,450	27,950	17,150	26,450	16,870	26,450	27,950
Annual Operating Cost	\$935,450	\$1,121,950	\$1,115,370	\$747,280	\$737,030	\$1,121,950	\$747,280	\$1,115,370	\$747,280	\$737,030	\$1,121,950	\$747,280	\$1,115,370	\$747,280	\$762,830	\$1,121,950	\$747,280	\$1,115,370	\$747,280	\$762,830
T/Y Acid Production	82,668	82,668	82,668	82,767	82,767	82,668	82,767	82,668	82,767	82,767	82,668	82,767	82,668	82,767	83,190	82,668	82,767	82,668	82,767	83,190
Production Cost/T	\$ 11.32	\$ 13.57	\$ 13.49	\$ 9.03	\$ 8.90	\$ 13.57	\$ 9.03	\$ 13.49	\$ 9.03	\$ 8.90	\$ 13.57	\$ 9.03	\$ 13.49	\$ 9.03	\$ 9.17	\$ 13.57	\$ 9.03	\$ 13.49	\$ 9.03	\$ 9.17
Control Cost/T	.15	.13	.05	.23	.10	.15	.23	.05	.23	.10	.15	.23	.05	.23	.05	.15	.23	.05	.23	.05

TABLE B-20
ACID MIST CONTROL COST FOR PROCESS 3.2.1
APPLIED TO
CLASS 1.1, 1.2 and 1.4 (SMELTER GAS) ACID PLANTS
FOR MIST CONTROL TO 0.5 mg/SCF FOR
NEW OR EXISTING OLFUM OR NON-OLFUM PRODUCING PLANTS

Process	3.2.1/1.2 (50)	3.2.1/1.1 (250)	3.2.1/1.2 (250)	3.2.1/1.4 (250)	3.2.1/1.2 (750)
Nominal Capacity	50 T/D	250 T/D	250 T/D	250 T/D	750 T/D
Production Rate	50.1 T/D	250.5 T/D	250.5 T/D	250.5 T/D	751.5 T/D
Conversion Rate	96 %	95 %	96 %	96.8 %	96 %
Initial Investment	\$485,000	\$1,185,000	\$1,185,000	\$1,790,000	\$2,205,000
Book Value	485,000	85,000	1,185,000	1,790,000	2,205,000
Raw Material and Utilities					
Sulfur	\$140,500	\$ 709,000	\$ 702,700	\$	\$2,107,000
S as SO ₂	9,800				117,600
Elec. Power	5,000	41,700	41,600	47,400	74,100
Cooling Water	70	24,700	24,700	47,900	74,990
Process Water	1,150	330	330	330	17,300
B. F. Water		5,770	5,770		
Steam	-12,800	- 64,200	- 64,200		- 192,500
Operating Expenses					
Labor	47,500	47,500	47,500	94,300	47,500
Supervision	21,100	21,100	21,100	21,100	21,100
Maintenance (4%)	19,400	47,400	47,400	71,700	88,000
Overhead @ 70% of Above	61,600	81,200	81,200	131,000	110,000
Indirect Costs					
Depreciation 10%)	85,000	11,450	207,000	314,000	386,000
Interest 7-1/2%)					
Taxes and Insurance (1-1/2%)	7,300	17,800	17,800	26,900	33,100
Annual Operating Cost	\$385,620	\$ 943,750	\$1,132,900	\$ 754,630	\$2,810,190
T/Y Acid Production	16,530	82,670	82,670	82,670	248,000
Production Cost/T	\$ 23.35	\$ 11.43	\$ 13.68	\$ 9.13	\$ 11.30
Control Cost/T	i.05	.26	.25	.33	.22

TABLE B21
ACID MIST CONTROL COST FOR SYSTEM 3.3.1
APPLIED TO
CLASS 1.2 ACID PLANT

Process	3.3.1/2.1 (250)
Nominal Capacity	250 T/D
Production Rate	250.49 T/D
Conversion Rate	96 %
Initial Investment	\$1,170,000
Book Value	1,170,000
Raw Material and Utilities	
Sulfur	\$ 702,700
S as SO ₂	
Elec. Power	47,500
Cooling Water	24,700
Process Water	330
B.F. Water	5,770
Steam	- 64,200
Ca(OH) ₂	3,800
CaSO ₄ (Waste)	880
Operating Expenses	
Labor	47,500
Supervision	21,100
Maintenance (4%)	46,700
Overhead @ 70% of Above	80,700
Indirect Costs	
Depreciation 10%)	205,000
Interest 7-1/2%)	
Taxes and Insurance (1-1/2%)	17,550
Annual Operating Cost	\$1,140,030
T/Y Acid Production	82,660
Production Cost/T	\$ 13.79
Control Cost/T	.36